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STONE AND WEBSTER/IONICS SO2 REMOVAL AND RECOVERY PROCESS. PHASE I

Wisconsin Electric Power Company

Prepared for:

National Environmental Research Center

May 1975

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STONE & WEBSTER/IONICS SO_2 REMOVAL AND RECOVERY PROCESS PHASE I FINAL REPORT

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The report covers Phase I of a potential three-phase program to evaluate the Stone & Webster/Ionics process at 1 MW pilot plant scale with the option to scale up and demonstrate process viability at the 75 MW prototype level. The report cites the objectives, approach, results, and conclusions, and discusses a program that included: the design, construction, and operation of, and completion of a test program for, the pilot plant; the design, construction, and testing of prototype-size electrolytic regeneration cells; the design, engineering, and estimation of construction and operating costs of the 75 MW prototype; and preparation of a test program and operating schedule for the prototype. An executive summary includes the background and objectives of the overall program and pilot-scale effort, and highlights significant results and conclusions. Although technical feasibility was demonstrated at the pilot scale, the economics of a 75 MW prototype plant at the site of the pilot plant do not appear favorable. There are no current plans to continue into Phase II (detailed design, procurement, and installation of the 75 MW prototype) or Phase III (12-month start-up and operational test period for the 75 MW prototype).

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PHASE I, FINAL REPORT

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231 West Michigan
Milwaukee, Wisconsin 53201

Contract No. 68-02-0297
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Prepared for

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TABLE OF CONTENTS

Section Page

EXECUTIVE SUMMARY xiii

PHASE 1A - PILOT PLANT OPERATION 1

1. ABSTRACT - PHASE 1A 1

2. CONCLUSIONS 2

3. RECOMMENDATIONS 4

4. INTRODUCTION 5

5. TEST PROGRAM OPERATING RESULTS 9
  5.1 Absorption-Stripping Section 9
  5.2 Electrolytic Cell Section 10
  5.3 Overall Conclusions 11

6. DISCUSSION OF PROCESS RESULTS 12
  6.1 Absorption 12
    6.1.1 SO2 Removal 12
    6.1.2 Mass Transfer Coefficients 12
    6.1.3 Caustic Utilization 15
    6.1.4 Entrainment 17
    6.1.5 Pressure Drop 18
    6.1.6 Particulate Removal, NOX and SO3 24
  6.2 Oxidation 26
    6.2.1 Literature Survey 26
    6.2.2 Data Reduction 27
    6.2.3 Results 30
    6.2.4 Discussion of Results 31
  6.3 Stripping 51
    6.3.1 Stripping Steam Rate 51
    6.3.2 Acid Addition 53
  6.4 Electrolytic Regeneration 58
    6.4.1 General Description of the Cell System 58
    6.4.2 Cell System Design Set Point 58
    6.4.3 Cell System Operations 63
    6.4.4 Initial Cell System and Process Debugging Period 63
    6.4.5 Cell System Evaluation Period 65
    6.4.6 Advanced Component Evaluation Period 69
  6.5 Process Material Balances 74
    6.5.1 Process Losses 74
    Loss Analysis Run Results 74
    Discussion of Results 75
  6.6 Cell Feed Treatment 79
    6.6.1 Contaminant Removal 80
    6.6.2 Major Stream Analysis 85

TABLE OF CONTENTS (CONT'D)

Section Page

6.6.3 Sources of Metal Contaminants 86
6.6.4 Cell Feed Liquor Conditioning in Future Installations 89

7. DISCUSSION OF OPERATING RESULTS 90
7.1 Process Consistency 90
7.2 Process Control 92
7.2.1 Absorption 92
7.2.2 Stripping 94
7.2.3 Feed Liquor Preparation 95
7.2.4 Cell Room 95
7.3 Materials of Construction 95
7.4 Equipment Operating Experience 95
7.4.1 SO2 Analyzer 95
7.4.2 Flowmeters 96
7.4.3 pH Meters 96
7.4.4 Temperature and Pressure Indicators 97
7.4.5 Level Control 97
7.4.6 Forced Draft Fan 97
7.4.7 Pumps 97
7.4.8 Absorption Tower 98
7.4.9 Stripper Column 98
7.4.10 Cell Room 98

8. DISCUSSION OF ANALTYICAL PROBLEMS 99
8.1 Basic Analysis Problems 99
8.1.1 NaHSO3/Na2SO3/NaHCO3/Na2CO3/NaOH Analyses 99
8.1.2 Na2SO4 107
8.2 Iron Analysis 109
8.3 Other Analyses 112

9. REFERENCES 114

10. APPENDICES 115
A. Limnetics, Inc. Report on Foreign Materials Analysis 116
B. Chronological History of Pilot Plant Operations 123
C. Oxidation Calculations 131
D. Sulfur Removal Calculations 133
E. British to Metric Conversion Table 135
F. Tabular Summaries and Measurements 136
G. IGT Trace Iron Analysis 148

Page

PHASE 1B - PROTOTYPE CELL DEVELOPMENT (DESIGN, FABRICATION, AND PERFORMANCE) 152

1. ABSTRACT 152

2. CONCLUSIONS 153

3. RECOMMENDATIONS 154

4. INTRODUCTION 155

5. DESIGN AND FABRICATION OF THE PROTOTYPE CELL COMPONENTS 156

6. PROTOTYPE CELL TEST FACILITY 160

7. PROTOTYPE CELL PERFORMANCE 166
    7.1 "A" Cell Performance 166
        7.1.1 Current Efficiency 166
        7.1.2 Energy Consumption 166
        7.1.3 Cell Voltage 169
    7.2 "B" Cell Performance 169
        7.2.1 Cell Voltage 169
        7.2.2 Current Efficiency and Energy Consumption 172

PHASE 1C - PROTOTYPE PLANT COST ESTIMATE, PROJECTED OPERATING COSTS, AND DESIGN AND CONSTRUCTION SCHEDULE 174

1. GENERAL DESCRIPTION OF PROCESS WORK 174

2. COST ESTIMATE FOR INCLUSION IN WEPCO 75MW POWER PLANT 175
    2.1 Design Basis Cost Summary Sheet (4250 lb SO2/Hr) 175
    2.2 Design Basis Cost Summary Sheet (3100 lb SO2/Hr) 175

3. PROJECTED MONTHLY OPERATING COSTS 178

4. DESIGN, ENGINEERING AND CONSTRUCTION SCHEDULE 181

TABLE OF CONTENTS (CONT'D)

Section **Page**

PHASE 1D - TEST PROGRAM AND OPERATING SCHEDULE FOR 75MW PROTOTYPE PLANT 183

1. INTRODUCTION 183

2. TEST PROGRAM OBJECTIVES 184
   - 2.1 Process Performance 184
   - 2.2 Absorption Section 184
   - 2.3 Stripping Section 186
   - 2.4 Feed Liquor Treatment 186
   - 2.5 Data Collection and Evaluation 186
     - 2.5.1 Technical Program 186
     - 2.5.2 Process Maintenance 187
     - 2.5.3 Process Operating Costs 187

ILLUSTRATIONS

Figure

PHASE 1A Page

I Stone & Webster/Ionics SO2 Recovery and Removal System - Simplified Block Diagram xvi

II Stone & Webster/Ionics SO2 Removal Pilot Plant - WEPCO, Valley Station, Milwaukee xvii

III Pilot Plant Absorber xviii

IV Pilot Plant Stripper xix

V Electrolytic Cell Module in Cell Room at Ionics, Inc. xxi

4.1 Pilot Plant Flow Diagram 7
6.1 Height of a Transfer Unit 14
6.2 Overall Gas Phase Mass Transfer Coefficient versus Superficial Gas Velocity 16
6.3 Entrainment from Stage 1 as a Function of Gas Rate 19
6.4 Entrainment from Stage 1 as a Function of Liquid Recirculation Rate 20
6.5 Entrainment from Quench Section as a Function of Gas Rate 21
6.6 Entrainment from Quench Section as a Function of Plate Water Flow 22
6.7 Pressure Drop through Absorption Tower 23
6.8 The Effect of Flue Gas Flow on Oxidation 32
6.9 The Effect of SO2 Inlet Concentration on Oxidation 33
6.10 The Effect of Total SO2 Removed on Oxidation 34
6.11 The Effect of Flue Gas Flowrate on the Net Draw Sodium Bisulfate Concentration 35
6.12 The Effect of SO2 Inlet Concentration on the Net Draw Sodium 36
6.13 The Effect of Total SO2 Removed on the Net Draw Sodium Bisulfate Concentration 37
6.14 The Effect of Absorber Net Draw Sodium Bisulfite Concentration on Oxidation 39
6.15 The Effect of SO2 Absorption Profile on Oxidation 40
6.16 The Effect of SO2 Absorption Profile on Oxidation (Total) 41
6.17 Mole Percent Sodium Bisulfite versus S/C Ratio 43
6.18 The Effect of SO2 Absorption Profile on Oxidation 44

ILLUSTRATIONS (CONT'D)

Figure		Page
6.19	The Effect of SO2 Absorption Profile on Oxidation (Total)	45
6.20	SO2 Removal in the Top Stage Versus Sodium Bisulfite Concentration in Top Stage Effluent	46
6.21	The Effect of Total Salt Concentration in Net Absorber Net Draw on Oxidation	47
6.22	The Effect of Gas-Liquid Contacting on Oxidation	48
6.23	The Effect of Heavy Metals Contamination on Oxidation	50
6.24	Limiting Stripping Steam as a Function of SO2 Removal	52
6.25	Excess Acid Residual SO2 in Stripper Bottoms as a Function of pH	54
6.26	Optimum pH for Stripper Bottoms Operation	56
6.27	Titration Curve - Sodium Sulfate Solution versus Water	57
6.28	Schematic Diagram of Electrolytic Cells	59
6.29	Design Point Material Balance for 56 Type "A" SULFOMAT Cells	61
6.30	Design Point Material Balance for 32 Type "B" SULFOMAT Cells	62
6.31	Design Cell Voltage - Current Density Relationships for Types "A" and "B" SULFOMAT Cells	64
7.1	Absorption Tower Response Testing	93
8.1	Distribution of Aqueous Sulfite Species as a Function of pH	100

PHASE 1B

Figure		Page
5.1	Cell Anode Assembly	159
6.1	Assembled Prototype Cell Stack	161
6.2	Design Point Material Balance for 16 Prototype "A" Cells	163
6.3	Design Point Material Balance for 16 Prototype "B" Cells	164
6.4	Design Cell Voltage - Current Density Relationships for Types "A" and "B" SULFOMAT Cells	165
7.1	Current-Voltage Curve for Prototype "A" Cells	170
7.2	Current-Voltage Curve for Prototype "B" Cells	171

PHASE 1C

Figure		Page
4.1	Proposed Construction Schedule for Prototype Plant	182

TABLES

Number Page

PHASE 1A

6.1 Particulates NOX and SO2 Levels on Absorber Inlet and Outlet 25
6.2 Bad Case Operating Conditions for Stripping Study 55
6.3 Selected Design Values of WEPCO Pilot Plant 60
6.4 Summary of WEPCO Pilot Plant Current Efficiency Measurements 66
6.5 Summary of Voltage-Current Data and Specific Energy Consumption Results in WEPCO Pilot Plant Cell System 70
6.6 Summary of "A" and "B" Cell Current-Voltage Data 72
6.7 Comparative Operating Conditions and Measured Losses 76
6.8 Cell Feed Specification 80
6.9 Profiles of SO2 and Fe in Feed Liquor between Stripper Drum and Cell Stacks during Initial Running with "Heavy" H2O2 Addition 83
6.10 SO2 and Fe Profiles in Major Streams of WEPCO Pilot Plant 84
6.11 Typical Fly Ash Analysis from WEPCO Valley Plant 87
6.12 Elemental Breakdown of Seven Typical Fly Ashes 88
7.1 Pilot Plant Operation and Availability 90
7.2 Absorption Tower Response Testing 94
7.3 Comparative SO2 Measurements 96
8.1 Sulfite-Bisulfite Determination 101
8.2 Bicarbonate in Absorber Liquid 108
8.3 Sodium Sulfate Analysis Gravimetric Determination 110
8.4 Iron Analyses in 3 N Sodium Sulfate Solutions 111
8.5 Total Sodium Analysis 113

PHASE 1B

5.1 Drawing List of Prototype Cell Components 157
6.1 Selected Design Values of Prototype Cell Test Facility 162
7.1 Summary of Performance Tests of Prototype "A" Cells 167

TABLES (CONT'D)

Number Page

7.2 Summary of Prototype "A" Cell Energy Consumption Data 168
7.3 Summary of Performance Tests of Prototype "B" Cells 173

PHASE 1C

2.1 Cost Summary Sheet for 4250 lb SO2/Hr Removal 176
2.2 Cost Summary Sheet for 3100 lb SO2/Hr Removal 177
3.1 Estimate of Operating and Maintenance Costs - 75 MW Demonstration Plant for 3100 lb SO2/Hr Removal 179

PHASE 1D

2.1 Test Program Objectives 185

EXECUTIVE SUMMARY

Stone and Webster Engineering Corporation (SWEC) in conjunction with Ionics, Incorporated, has designed and engineered a process for the removal and recovery of sulfur dioxide from stack gases. In July 1972, EPA and Wisconsin Electric Power Company (WEPCO) initiated a potential three phase program to evaluate the SWEC/Ionics process at pilot plant (1MW) scale with the option to scale-up and demonstrate process viability at the prototype (75MW) level. The flue gas SO2 removal and recovery process employs electrolytic regeneration of the working fluids. It considerably reduces solids handling and disposal problems inherent in lime/limestone slurry systems and offers operational advantages for utilities over other regenerable systems. This report covers Phase I of the contract.

The overall goal of Phase I work was to provide information for the design, construction, and operation of a 75 MW Prototype Plant using the Stone & Webster/Ionics SO2 Removal Process. This goal was accomplished by means of the following steps:

Phase 1A - Design, construct, and test operate a Pilot Plant sized at approximately 1 MW. The results are summarized as follows:

1. The plant was built and operated successfully, demonstrating feasibility of the process. Information was obtained on the mechanical operability and reliability of equipment.
2. The performance of the electrolytic cells was demonstrated successfully in an industrial environment.
3. The effects that process variables have on process performance were determined.

Phase 1B - Design, construct, and test commercial size electrolytic regeneration cells which would be suitable for use in a 75 MW Prototype Plant. The results of this effort were:

1. Cells were designed, constructed, and tested, demonstrating a five-fold increase in capacity over the Pilot Plant cells at the same or a lower energy factor.
2. Mechanical integrity of the larger cell units was demonstrated.
3. Component designs were developed that simplified field assembly of the electrolytic cells.

Phase 1C - Design a 75 MW Prototype Plant to be installed at Wisconsin Electric Power Company's Valley Station site and establish estimates of capital and operating costs. The results were:

1. The design of the plant at the specified locations was completed.
2. Cost estimates for construction of this plant were established for two design capacities.
3. Operating cost for a one year operating and testing program following plant start-up was estimated.

Phase 1D - Develop a test program and operating schedule for the 75 MW Prototype Plant. The results of this effort were:

1. An orderly operating schedule was established for start-up and testing of the 75 MW plant.
2. A test program was established designed to supply data which could not be obtained from the Pilot Plant operation.

Each of these steps is discussed in corresponding sections of this report. This Executive Summary gives an overview of the Phase I results.

PHASE IA, DESIGN, CONSTRUCTION, AND OPERATION OF THE PILOT PLANT

Operation of the Pilot Plant provided data to form a basis of work for the other parts of Phase I. The Pilot Plant was constructed and installed at WEPCO's Valley Station in Milwaukee (Figures I & II). The plant was designed to remove more than 90 percent of the SO2 from flue gas flowing at 2200 (actual) cubic feet per minute.

Pilot Plant Design Criteria

Flue Gas Flow	2200 Ft^3 /Min
Flue Gas SO2 In	2000 PPM
Flue Gas SO2 Out	200 PPM

This would be roughly equivalent to the flue gas from a boiler with a capacity of about 0.75 MW. Design of the Pilot Plant progressed satisfactorily; there was no design procedure which was beyond proven practice. Construction encountered the equipment delivery and cost inflation problems experienced by the entire industry during 1973. The Pilot Plant was commissioned in June 1973. After overcoming some typical shakedown difficulties, the test program was carried out and the technical feasibility of the process was established. An important part of the establishment of feasibility was demonstrating the operability of individual process steps. These results are reviewed below.

The absorber, shown in Figure III, demonstrated SO2 removal efficiencies of 90 percent or more at SO2 inlet concentrations of up to 3600 ppm. This was accomplished in two ten-foot packed stages. An average of 13 percent of the absorbed SO2 was oxidized in the Pilot Plant ("oxidation" raises both the capital and operating costs of most regenerable processes and should generally be minimized). The effects of several parameters on oxidation in the absorber were studied as part of the test program. It was found that oxidation was lowered by shortened gas/caustic solution contact times and by increased sodium bisulfite concentrations in the absorbing solution. Early problems of overhead entrainment and quench water carryover in the absorber were also resolved.

The stripper, shown in Figure IV, satisfactorily removed SO2 from the absorbing solution with steam after that solution was acidified to pH 2.5 to 3.0 with recycled acid sulfate. The stripper's internal steam requirements were found to be 1.5 to 2.0 pounds per pound of SO2, depending upon the precise condition of the stripper bottoms and the efficiency of the packing. Some unanticipated operating difficulty was experienced that was particular to the installed stripper equipment. Future designs should eliminate this difficulty.

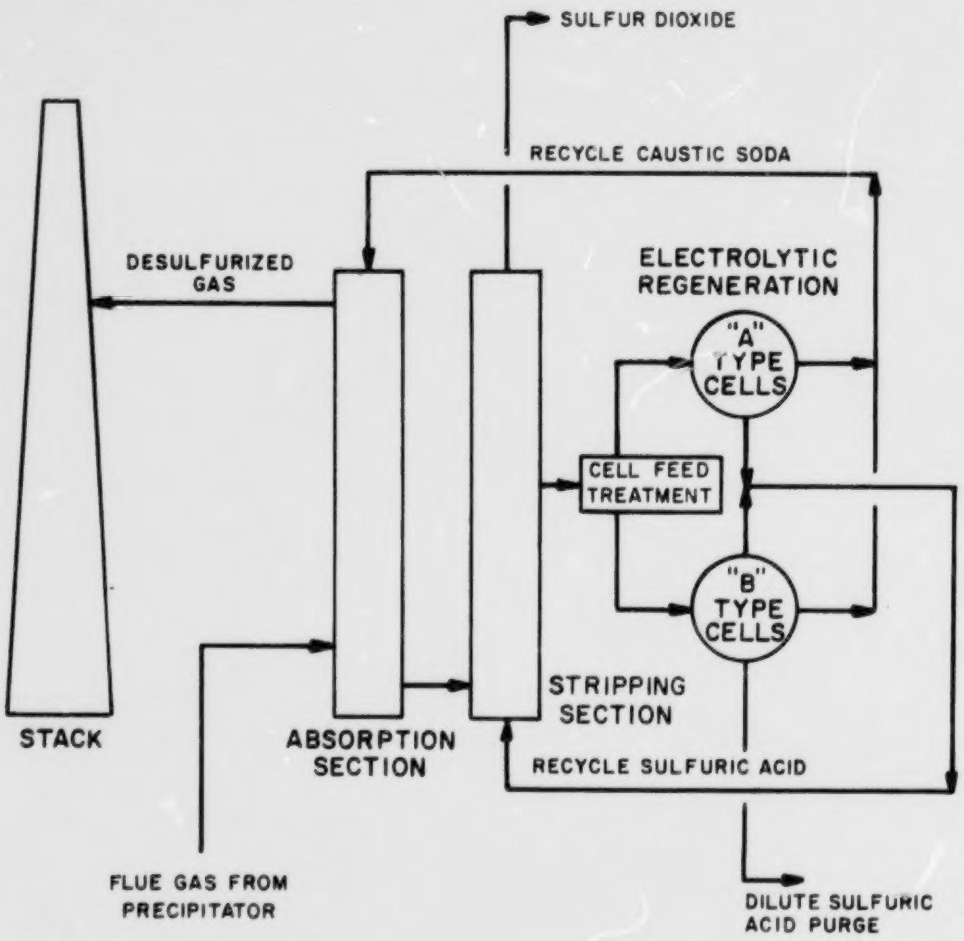
SULFUR DIOXIDE
RECYCLE CAUSTIC SODA
DESULFURIZED GAS
ELECTROLYTIC REGENERATION
"A" TYPE CELLS
CELL FEED TREATMENT
"B" TYPE CELLS
STRIPPING SECTION
STACK
ABSORPTION SECTION
RECYCLE SULFURIC ACID
FLUE GAS FROM PRECIPITATOR
DILUTE SULFURIC ACID PURGE

FIGURE I. STONE & WEBSTER/IONICS SO_2 REMOVAL PROCESS

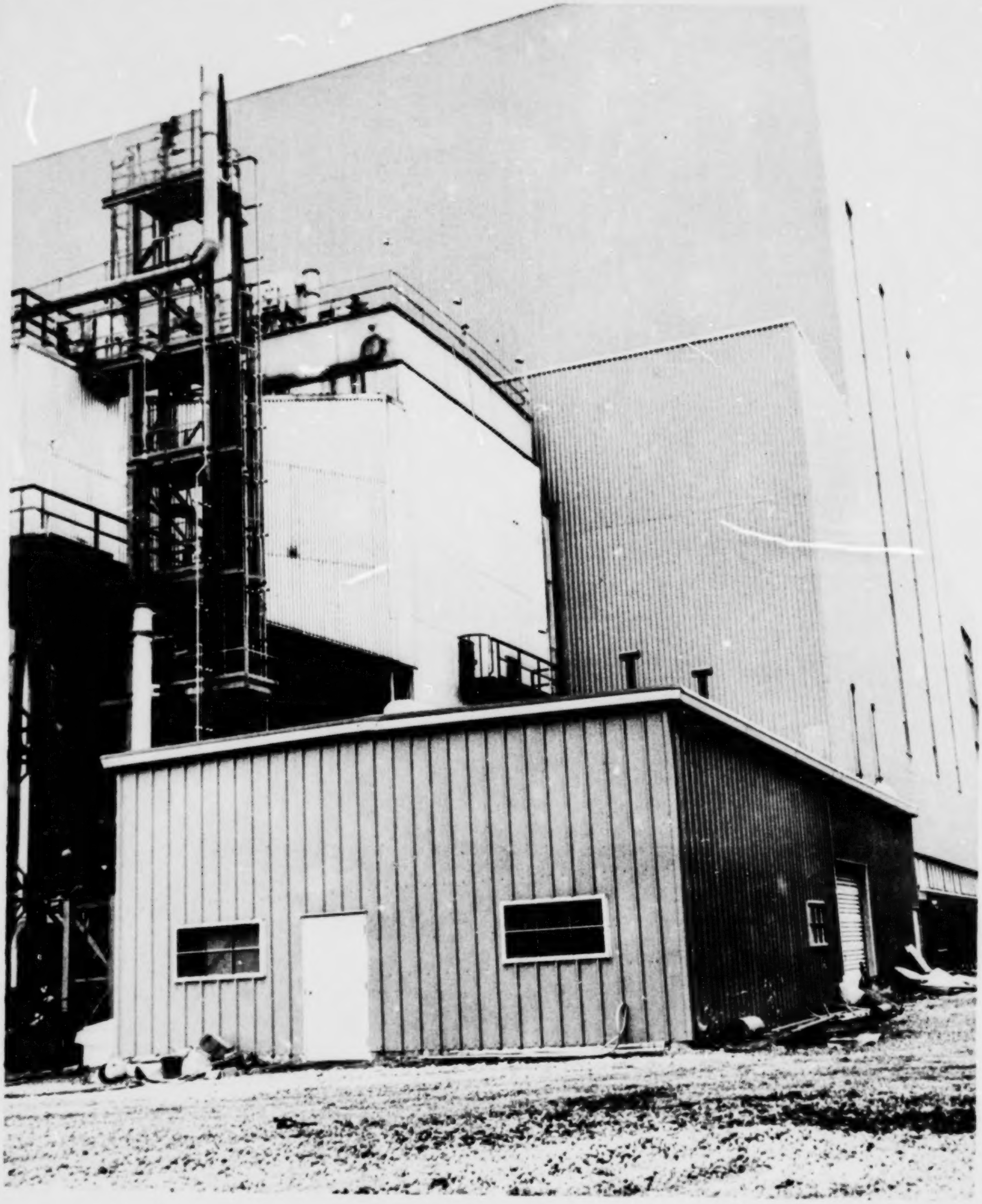

FIGURE II. STONE & WEBSTER / IONICS SO_2 REMOVAL PILOT PLANT – WEPCO, VALLEY STATION, MILWAUKEE

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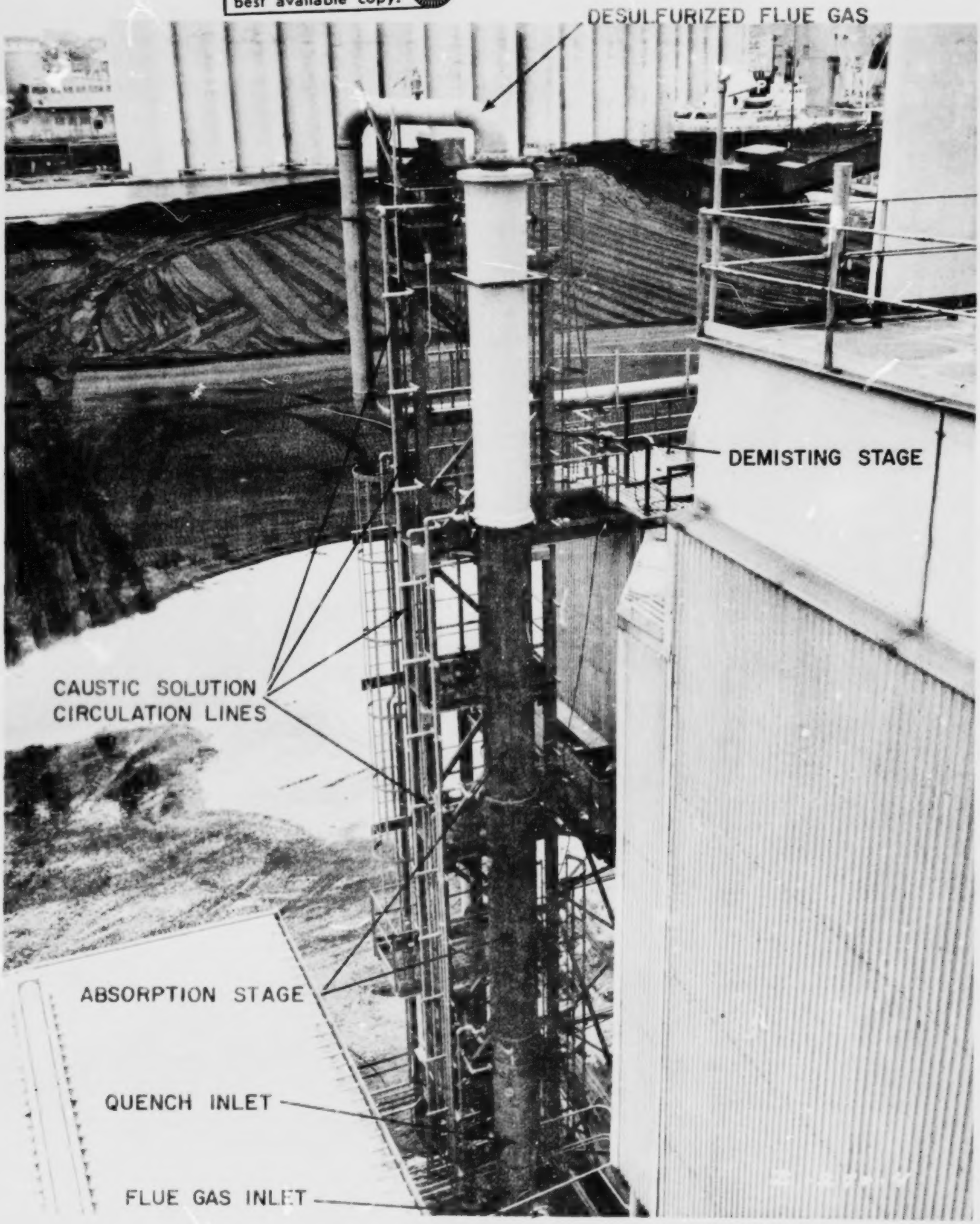
DESULFURIZED FLUE GAS
DEMISTING STAGE
CAUSTIC SOLUTION
CIRCULATION LINES
ABSORPTION STAGE
QUENCH INLET
FLUE GAS INLET

FIGURE III. PILOT PLANT ABSORBER

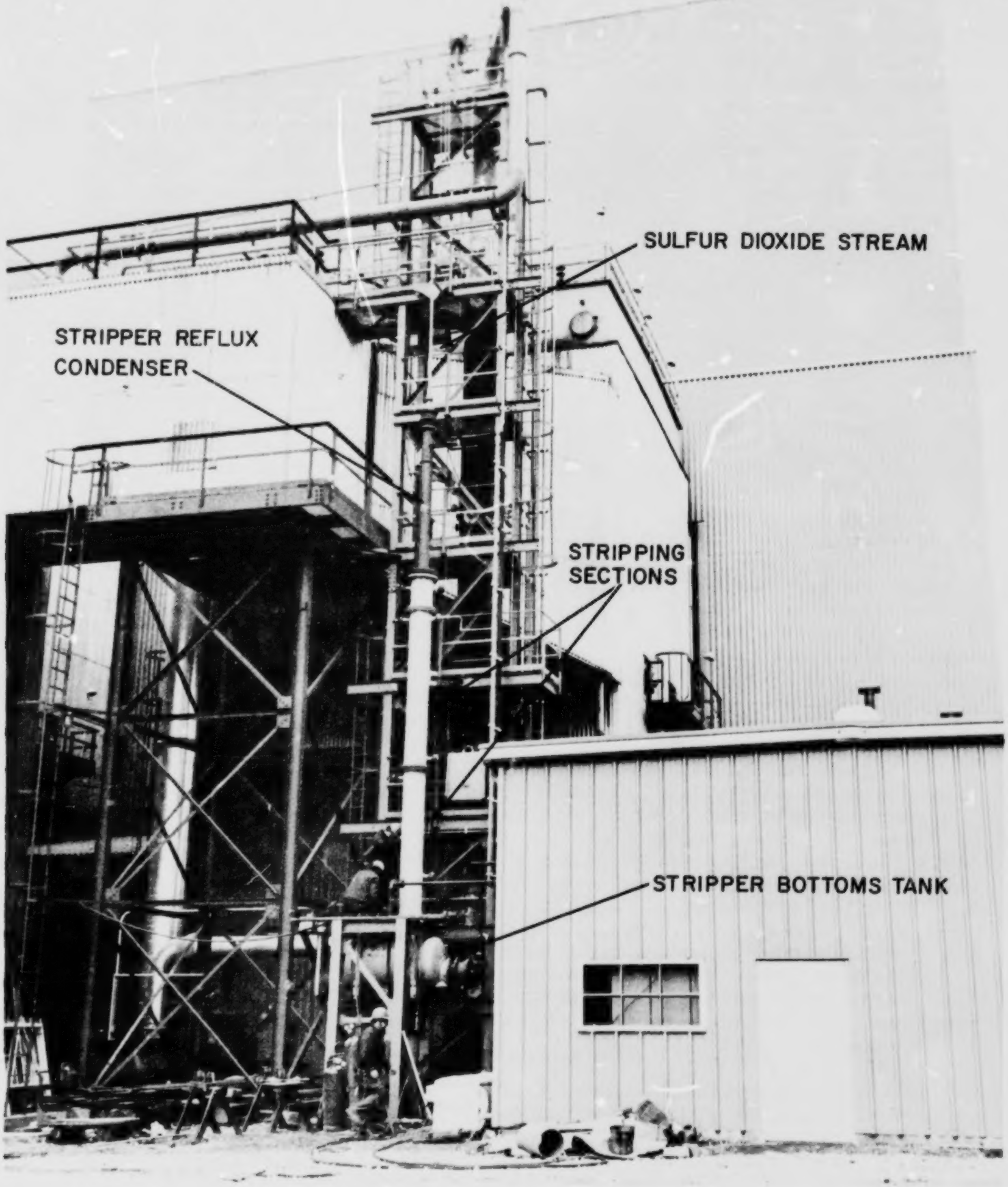
SULFUR DIOXIDE STREAM
STRIPPER REFLUX CONDENSER
STRIPPING SECTIONS
STRIPPER BOTTOMS TANK

FIGURE IV. PILOT PLANT STRIPPER

The Pilot Plant's cell feed was kept sufficiently free of contaminants (heavy metal cations and chloride ions) by a series of treatment steps. Oxidation by hydrogen peroxide addition followed by pH adjustment to 8-9 precipitated most contaminants and allowed their removal in a filtration step. The dissolved iron was reduced to less than 0.1 mg/l in this manner. The oxidation step was at first attempted with a manganese zeolite bed which failed due to the higher than anticipated concentration of oxidizable material in the stripper bottoms. This system operated consistently well, however, after the beds were replaced by the peroxide addition. Simple aeration may give the same results as peroxide addition, but that requires further study.

The electrolytic cells (shown in Figure V) regenerated the caustic and acid solutions used in the process. This was accomplished by applying an electric charge across a stack of cell compartments, containing the cell feed liquor, separated by membranes which selectively passed ions of positive or negative charge. The membranes were arranged to regenerate acid or caustic solutions in alternating compartments down the length of the stack. Oxidation in the absorber and other parts of the process produced nonregenerable sulfate which was purged by special cells, with an extra membrane, as dilute, about 10 percent, sulfuric acid. The rate of production of this acid was directly proportional to the rate of oxidation. The pilot plant cells had shakedown operating difficulties that were related to inadequate feed treatment and the use of "off-spec" caustic soda, which contained chloride, for sodium replacement. It was also found that the sodium sulfate concentration in the cell feed should be less than 3.5N (Normal) to prevent crystallization in the cells. Once these difficulties were resolved and the limiting operating conditions found, the cells operated reliably and exceeded design efficiency in normal operating conditions.

It was also found that use of "inert" anodes rather than those of lead alloy would reduce electric power consumption costs, an observation that was used in estimating the Prototype Plant costs in Phase IC. The energy required for operation of cells using inert anodes in the 75 MW plant was scaled from results obtained with the Pilot Plant. Scale-up requirements were verified during testing of the Prototype Cells in Phase IB.

The estimated operating costs for the 75 MW Plant were $60,000/Year lower than for an equivalent plant with lead anodes. The estimated initial investment was about $100,000 higher with inert anodes, but the reduced operating costs could repay this difference rapidly.

Calculations predicted that 4500 kw (6.0 percent of 75 MW capacity) would be required to operate the Prototype Plant cells and 1433 kw (1.9 percent of 75 MW capacity) would be needed for other process equipment. The total energy requirement for this installation at the Valley Plant of WEPCO was estimated to be 7.9percent of the 75 MW capacity.

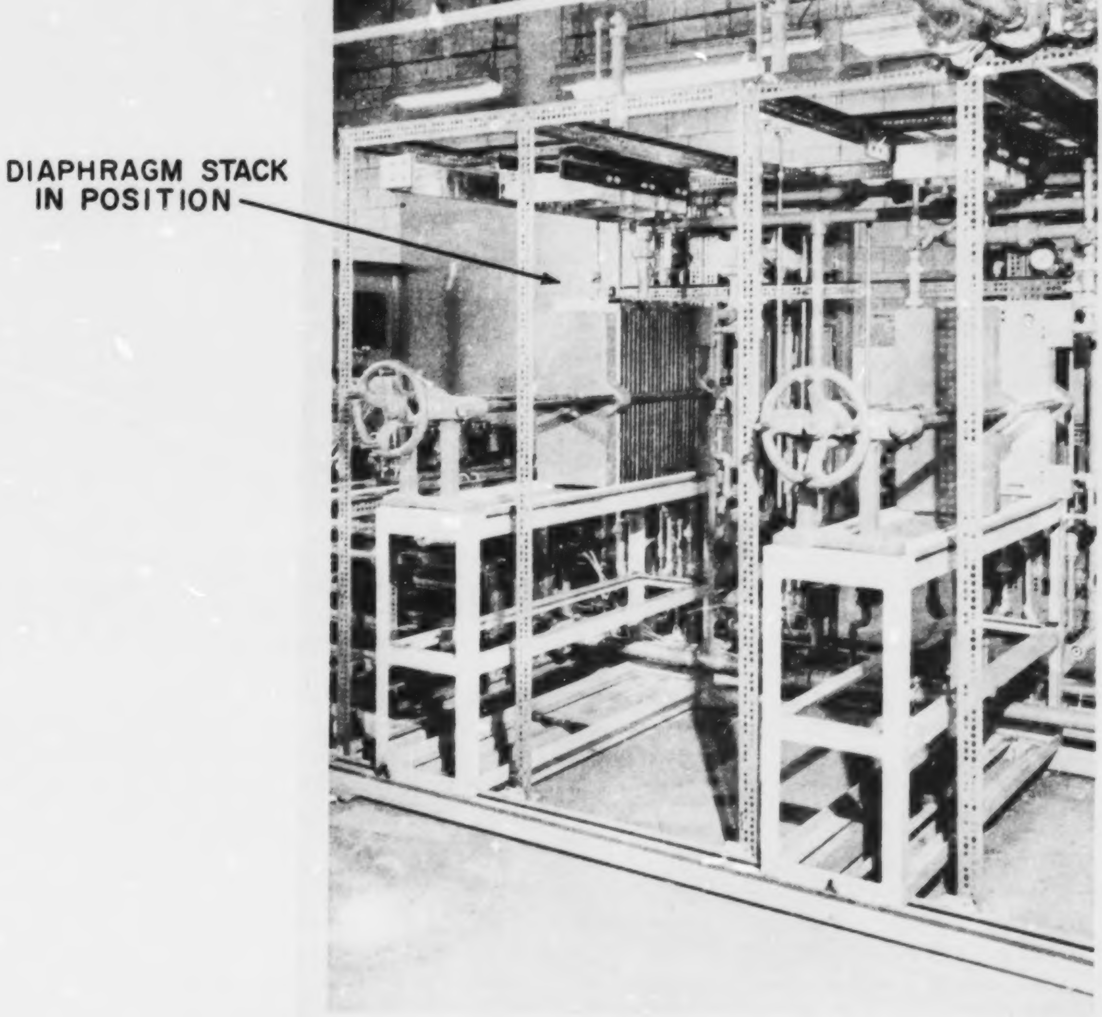
DIAPHRAGM STACK IN POSITION

FIGURE V. ELECTROLYTIC CELL MODULE IN CELL ROOM AT IONICS, INC. BEFORE PILOT PLANT INSTALLATION

The Pilot Plant achieved closed loop operation. This was indicated by closure of the sodium balance around the system and demonstrated the feasibility of operation in the regenerable mode. During the course of the Pilot Plant's operation, specific studies were also made of the overall material balance.

MATERIAL BALANCE SUMMARY FOR MAJOR PROCESS SPECIES, %*

Species	Present in Process Streams	Accounted for in Mechanical or Handling Losses	Unaccounted for
Na+	97.8%	2.2%	0.0%
SO3	97.9%	2.1%	0.0%
H2O	94.3%	1.3%	4.4%

Water was lost in the Pilot Plant operation, but test procedures determined at which points it was being lost. A large amount was apparently used to saturate the flue gas in the absorber; hence, a more effective quench water system upstream of the absorber would be used in the Prototype Plant. Losses can be more easily monitored in the Prototype Plant, once having been identified and located in the Pilot Plant work.

In addition to the process related experience, mechanical requirements for the process equipment were determined. Based upon Pilot Plant experience, equipment of improved design and materials of construction has been specified in Phase IC work. Rotating equipment specifications and operation procedures which increase operating reliability have particulary been determined. Sample metal coupons were placed in several environments in the process and examined upon completion of the Pilot Plant's testing schedule. Material of construction specifications based upon coupon examination have been used in the design and engineering work of Phase IC.

The Pilot Plant demonstrated the overall operability and technical feasibility of the SWEC/Ionics SO2 process. Further Pilot Plant work is not required. Process experience can now advance only with a larger unit. The Pilot Plant work has identified the following specific objectives for the Prototype Test Program:

1. Utility-type mechanical reliability should be demonstrated for all pieces of equipment.

2. A quantitative water balance should be made.

3. Operation of the stripper should be more precisely characterized.

4. The use of large-scale equipment in the Cell Feed Treatment system should be demonstrated and air oxidation should be studied for use in place of the peroxide addition.

*Percent of species in daily cell feed

5. Parameters affecting oxidation in the absorber which should be studied are packing type and volume, and flue gas oxygen concentration.

PHASE IB, DEVELOPMENT OF PROTOTYPE ELECTROLYTIC CELL SYSTEM

Prototype cell development was carried out in the laboratories of Ionics, Incorporated. Cell assemblies suitable for use in the Prototype Plant were designed, fabricated, and tested under simulated process conditions. The Prototype cells were scaled up to a production capacity per cell in excess of five times the capacity of the Pilot Plant cells. Emphasis was placed on development of a prefabricated "cell package" for easy assembly and disassembly.

Particular problems of scale-up which were resolved within this context included achieving adequate flow distribution in the cells, obtaining a recirculation rate for the electrode compartment high enough to allow disengagement of the gas produced, and construction of a unit that avoids exposure of the electrodes to the process solution in the cell manifolds. One type of cell assembly experienced some leakage externally and internally early in the program, but this was corrected by minor modifications which would be incorporated into existing production molds for components in the future.

The Prototype cell performance met the design criteria of the contract. There was no loss of current efficiency with the increased size. This demonstrates that the cell operation is understood well enough to be scaled-up confidently and indicates that the cells are ready to be demonstrated in the Prototype Plant. These cells should be installed and operated as part of an actual process application as the next step in their development.

PHASE IC, PRELIMINARY PROTOTYPE PLANT ENGINEERING DESIGN

Work in Phase IC included the design, engineering, and preparation of a cost estimate for a Prototype Plant to be installed at WEPCO's Valley Station. This plant would remove SO2 from flue gas exiting Boilers 3 or 4 which have individual capacities of about 75 MW. Projected costs for operating the unit and carrying out the test program outlined in Phase ID were tabulated for each of the 12 operation and test months.

Two cost estimates were prepared for design and construction of the Prototype Plant. These estimates are detailed in Tables 2.1 and 2.2 in Phase IC, pages 214 and 215 herein. One was based on removal of 4250 lbs SO2/hr for operation of the cells on "off peak" hours only and the other on 3100 lbs SO2/hr for continuous cell operation. The practical minimum design basis is 3100 lbs SO2/hr. This represents the highest average SO2 absorption over a one-month period (February) during 1973, the latest year from which complete coal consumption and sulfur content data for the Valley Plant were available. This design capacity must be considered as minimum even though it is more than enough for the remaining months. Short-lived increases of SO2 removal rates above the average rate for the entire year can be handled by the system's storage capacity, but it would be impractical to supply the large storage capacity needed to spread regeneration necessitated by a month-long surge over other months. The overall costs tabulated were $14.475 MM for the 4250 lb SO2/hr plant with an automated cell room, and $12.229 MM for the 3100 lb SO2/hr plant with a semiautomatic cell room. The estimates are higher than those generated at the inception of this contract due in part to the rapid escalation in materials, equipment, and labor costs in the intervening period.

The Phase IC costs are specifically related to the Valley Station site and reflect severe space and retrofit limitations which require intricate arrangement of equipment. It is anticipated that the costs for this unit at a more adaptable or new site would be lower. Also reflected in these estimates is the expense of including the equipment flexibility and instrumentation necessary to conduct the Test Program (Phase ID). An operating plant would not require such cost-raising extras, but with them, this Prototype Plant could provide data for design optimization and accurate prediction of large scale equipment costs.

The operating and maintenance costs similarly reflect the fact that the Prototype Plant will be a test facility for most of the time covered by the program. (Refer to Table 3.1, Phase IC) page 220. A large technical support effort will be required for start-up and operation during the test program. This period is expected to require spending about $156,000 per month (wages and prices February, 1975, no credit for by-products) in operating costs. However, when normal operation ensues, the monthly costs are expected to be about $102,000 per month. If credits for condensate returned and by-products are taken, the costs could be as low as $97,000 per month during the test program and $43,000/month during normal operation if the current market for SO2 hold (February 1975 basis).

It should be pointed out that the indicated favorable economics of by-product credits would probably not hold true for a large scale installation. Conversely, capital costs per kw capacity would decrease for a larger plant.

PHASE ID, TEST PROGRAM AND OPERATING SCHEDULE FOR 75 MW PROTOTYPE PLANT

Phase ID included planning the operation of the SO2 Removal Prototype Plant and specifying test objectives. The SO2 Removal Plant has no polluting effluents and therefore, inherently meets all operating codes and legal restraints. Marketing surveys by SWEC have shown that there is a market for the SO2 produced. Dilute acid produced by the process could be used to regenerate the demineralizer water units of the WEPCO power plant. There is a relatively small amount of filter cake from the cell feed liquor treatment which could be disposed of with the ash from the boilers. The sulfur dioxide would be sold as a process by-product. Although the disposition of by-products appears favorable for the 75 MW Prototype Plant, this condition cannot be readily forecast for a full scale installation. Complete mechanical testing is planned before process operation is begun.

The test program will extend study in several areas which could not be completely studied in the Pilot Plant Program. Water loss by saturation of the flue gas and/or entrainment overhead will be studied in the absorption section. The effect of NOx, heavy metal cations, SO3, and flue gas O2 concentrations on oxidation will be studied, especially in the absorber. The minimum stripping steam for residual SO2 concentration in the stripper bottoms effluent will be determined. The economic optimum SO2 concentration in the solution from the stripper bottom will then be known in terms of stripping steam economy. Cell feed liquor treatment using peroxide addition and filtration will also be tested. All data will be evaluated to provide equilibrium and equipment correlations for scale-up use. Accurate records of process maintenance will be kept to determine the proper application of estimating techniques. Process operating costs will be kept in detail to provide a basis from which to project costs to units larger than 75 MW.

RECOMMENDATIONS

SWEC and Ionics believe that the results of the Phase I work justify evaluation of this process on a commercial scale. WEPCO has decided that the difficulties and costs of retrofitting a 75 MW prototype installation at the site of the Pilot Plant cannot be justified at this time. The Pilot Plant results indicate the SWEC/Ionics SO2 Removal Process is technically feasible. Accurate data for prediction of capital and operating costs for a 500 MW plant can only be obtained by the construction and operation of a Prototype Plant.

PHASE 1A

PILOT PLANT OPERATION

I

ABSTRACT-PHASE 1A

The first phase of the EPA-WEPCO sponsored program to evaluate the Stone & Webster/Ionics closed cycle SO2 removal system has been successfully completed. The technical feasibility of the process was demonstrated on a 2200 ACFM pilot plant by meeting emissions and operating requirements over a representative range of conditions. The average SO2 removal was 85-95 percent at exit concentrations of 200-300 ppm SO2. Oxidation of SO2 in the absorber averaged 3.4 lb/hr* or 13 percent of the SO2 removed. The data and experience obtained will allow for the design and operation of a reliable prototype unit. The test program also has defined areas requiring further study beyond the scope of this work, which will permit additional design optimization when their effects are fully determined.

(*) Metric conversions may be found in Appendix E, British-to-Metric Conversion Table.

II

CONCLUSIONS

The following conclusions were reached from the operation of a 2200 ACFM Stone & Webster/Ionics SO2 removal system pilot plant.

1. The technical feasibility of the process was demonstrated.
2. SO2 removal efficiencies of 90 percent or more (for SO2 inlet concentrations up to 3600 ppm) were attained with two 10 foot packed stages.
3. The process was operated at oxidation levels less than 15 percent.
4. Minimum oxidation was favored by minimizing gas-liquid contact residence time and maximizing sodium bisulfite concentration in the absorbing liquor.
5. High sodium bisulfite concentration was favored by high inlet SO2 concentration.
6. Gas rate and total salt concentration had little effect on oxidation.
7. The overall energy consumption per mole of caustic produced by the electrolytic cells was lower than the design objective.
8. Cell production capacity exceeded the design objective.
9. Closed loop operation was achieved as indicated by closure of the sodium material balance.
10. The vapor pressure relationships for the aqueous sodium sulfite-bisulfite-sulfate system agreed with the data of Johnstone*. Sodium sulfate concentration did not affect SO2 vapor pressure over the solution.
11. The pH of the stripper bottoms effluent should be controlled to between 3.2 and 3.5 to optimize recycle caustic consumption and SO2 stripping.
12. Stripping steam requirements in the pilot plant were between 1.5 and 2.0 pounds per pound of SO2 removed, exclusive of process preheat which was

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*See Section 9, References.

estimated to be 4.25 pounds per pound of SO2 for the pilot plant.

13. The maximum concentration of sodium sulfate in the cell feed liquor should be 3.5 normal in order to avoid crystallization.

14. The heavy metal cation specifications for cell feed liquor were met using a combination of hydrogen peroxide addition and filtration.

15. Process water losses can be expected; they are contingent on process design and maintenance. In the pilot plant water losses varied from 60 to 200 gallons per day attributable to electrolysis, humidification, and operating losses.

16. Operating problems with the pilot plant were mainly mechanical. Improved equipment and materials selection will minimize operating difficulties in future plants.

III

RECOMMENDATIONS

In order to establish commercial feasibility and costs, the process should be demonstrated on a prototype plant scale of at least 75 to 150 MW. Items to be studied more closely during that period should include:

1. Maintenance and Operability

   The most important facet that requires demonstration is the mechanical operability of the process. Process oriented problems are minor compared to the need to demonstrate utility-type reliability from rotating equipment, commercial sized cell components, and other items of equipment.

2. System Water Balance

   The water balance for the pilot plant was inconclusive. Evaporative losses from the cells, the absorber, stripper, and various tanks should be monitored in order to establish specific rates.

3. Stripping Section

   The lack of reliable flowmeters around the pilot plant stripper prevented the measurement of stripping rates for the SO_2-Na_2SO_4-H_2O system. The stripping steam rate, mass transfer coefficients, and pH relationships within the tower require additional study.

4. Feed Liquor Preparation

   The demonstration of large scale feed liquor treatment is needed including the use of precoat filters and their effectiveness in removing small quantities of iron and aluminum hydroxide. Additionally, the use of air oxidation in place of peroxide addition should be investigated.

5. Oxidation

   Areas not investigated during the test program, but worthy of study with the objective of reducing oxidation, are the effects of packing type and volume and the effect of oxygen concentration on oxidation.

6. Trace Elements

   A study of the **buildup** of trace elements and means for their removal should be made.

IV

INTRODUCTION

The present annual emission rate of sulfur dioxide into the atmosphere in the United States is estimated at nearly 40 million tons. Approximately 60 percent of this is emitted from the stacks of power stations which burn fossil fuels as primary energy sources. Roughly two-thirds of this, or approximately 40 percent of the total, is from stations which burn coal. Removal of SO2 from stack gases is a feasible method which may be used to abate these emissions.

Stone & Webster Engineering Corporation, in conjunction with Ionics, Inc., has designed and engineered a process for the removal and recovery of sulfur dioxide from stack gases based on the absorption of sulfur dioxide in an alkaline solution which then is regenerated. The key component of this process is the Ionics electrochemical cell which regenerates the spent absorbent.

The Stone & Webster/Ionics SO2 removal process is applicable to gaseous effluents from stationary power plants burning fossil fuels containing sulfur and to tail gases from sulfur recovery plants, smelters, and sulfuric acid plants.

The principal advantages of this process are:

1. Very small amounts of makeup chemicals are required and no secondary waste products are generated which represent additional contamination to the environment. A relatively small dilute sulfuric acid purge stream is pure and may or may not represent a penalty to the process.
2. Flue gas SO2 content can be reduced to a minimum level since NaOH is the absorbent and SO2 has negligible vapor pressure over a caustic solution.
3. The process chemistry is simple and well known.
4. The components in the regenerating electrolytic cell system are readily mass produced and can be improved through evolutionary engineering development even after installation.
5. The modular cell operation enables cell regeneration to fluctuate with boiler operation without loss of efficiency.

In order to evaluate this process in a realistic manner, a pilot plant was installed at Wisconsin Electric's Valley

Plant in Milwaukee, to process 2200 acfm of flue gas at an inlet SO_2 concentration of 3600 ppm. This is approximately equivalent to flue gas from a power plant of 0.75 Mw capacity. The concentrated SO_2 stream was returned to the stack since there was no need to demonstrate SO_2 recovery technology.

The primary goals of the test program were to:

1. Demonstrate the system operability and reliability from both a process and mechanical standpoint.
2. Measure cell performance in an industrial environment.
3. Determine the effects of process variables on oxidation.

Oxidation has a direct effect on the power requirements for the system as well as the initial capital investment, because it increases the amount of caustic to be produced by regeneration and the number of "B" cells (more expensive) required to purge sulfate ions.

This report summarizes the pilot plant operating experience and results obtained during the period from July 1973 to June 1974.

The Stone & Webster/Ionics SO_2 removal process pilot plant is shown in Figure 4.1. It is a closed loop system for removing sulfur oxides from gas streams. The acid gases are initially absorbed by sodium hydroxide in a packed tower. The resultant sodium sulfite-sodium bisulfite solution is acidified with sulfuric acid. Sodium sulfate is formed and the released SO_2 is stripped from the process liquor for recovery. The acid and caustic feed chemicals are regenerated by splitting the sodium sulfate product in an electrolytic cell system.

The process can be summarized by the following reaction sequence:

1. ABSORPTION

$$2\,NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$$
$$Na_2SO_3 + SO_2 + H_2O \longrightarrow 2NaHSO_3$$

2. ACIDIFICATION

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2O + SO_2$$
$$2NaHSO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O + SO_2$$

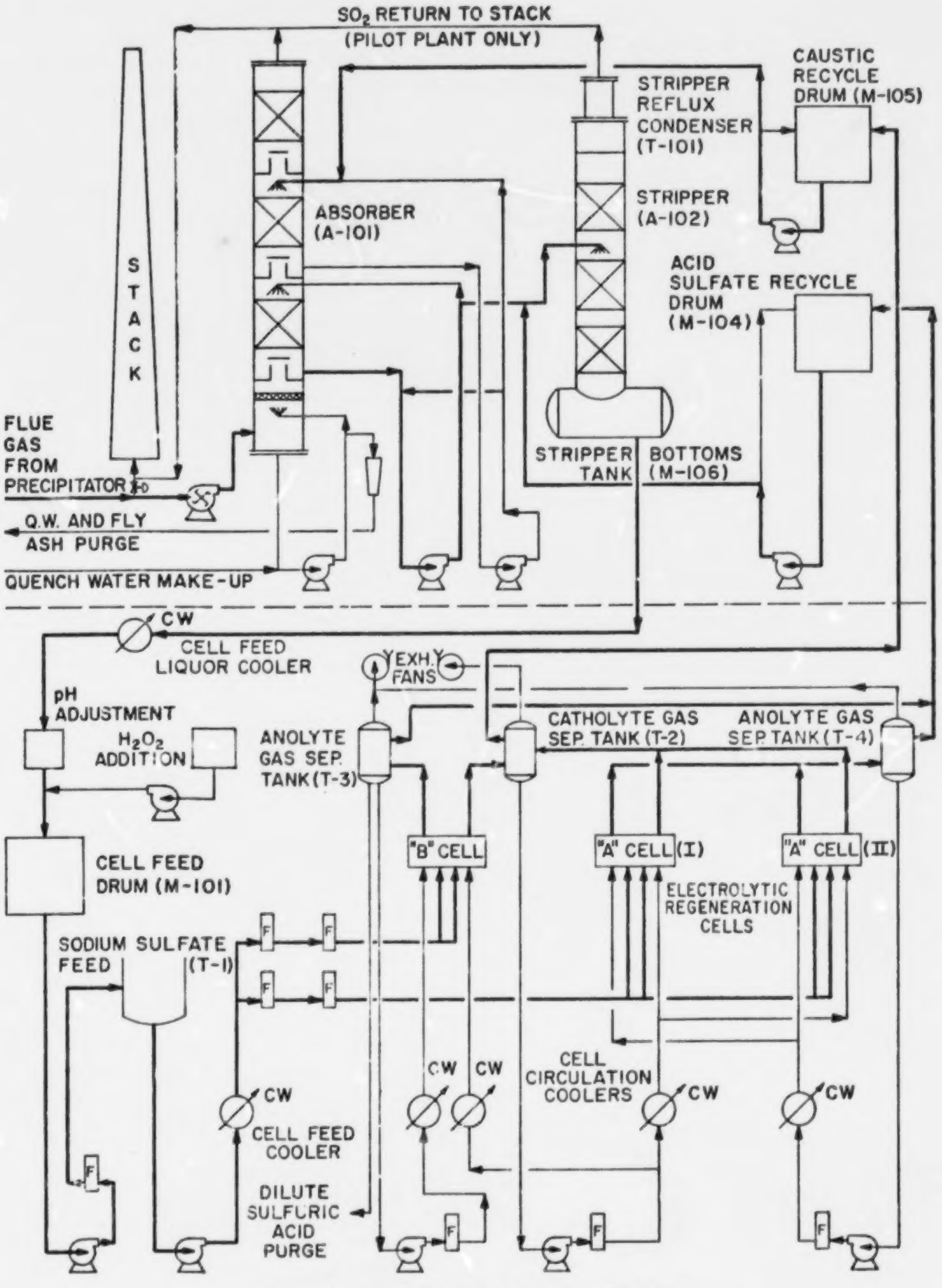

SO$_2$ RETURN TO STACK
(PILOT PLANT ONLY)
CAUSTIC RECYCLE DRUM (M-105)
STRIPPER REFLUX CONDENSER (T-101)
STRIPPER (A-102)
STACK
ABSORBER (A-101)
ACID SULFATE RECYCLE DRUM (M-104)
FLUE GAS FROM PRECIPITATOR
STRIPPER BOTTOMS TANK (M-106)
Q.W. AND FLY ASH PURGE
QUENCH WATER MAKE-UP
CW
CELL FEED LIQUOR COOLER
EXH. FANS
pH ADJUSTMENT
H$_2$O$_2$ ADDITION
ANOLYTE GAS SEP. TANK (T-3)
CATHOLYTE GAS SEP. TANK (T-2)
ANOLYTE GAS SEP. TANK (T-4)
"B" CELL
"A" CELL (I)
"A" CELL (II)
ELECTROLYTIC REGENERATION CELLS
CELL FEED DRUM (M-101)
SODIUM SULFATE FEED (T-1)
F
CW
CW
CW
CELL CIRCULATION COOLERS
CW
CW
CELL FEED COOLER
DILUTE SULFURIC ACID PURGE

FIGURE 4.1 - SCHEMATIC FLOW DIAGRAM OF FINAL VALLEY STATION PILOT PLANT

3. REGENERATION

$$Na_2SO_4 + 2H_2O + E \longrightarrow 2NaOH + H_2SO_4$$

The primary side reaction is the absorption of sulfur oxides as SO_3 either by direct absorption or by the oxidation of sulfites and/or bisulfites. This will form sulfate directly and the sulfur oxides will not be released upon acidification, thereby resulting in a net sulfate increase within the system. Special electrolytic cells are used to purge this excess sulfate as dilute sulfuric acid.

The electrolytic cell system consists of two types-designated as types "A" and "B". "A" cells consist of two diaphragms and a cation membrane. The sodium sulfate feed is split into mixed caustic ($NaOH$ and Na_2SO_4) and mixed acid (H_2SO_4 and Na_2SO_4) streams for use directly in the process. Conversions are kept low to increase cell efficiency. "B" cells are similar to "A" cells except that they contain an anion membrane in addition to the other components. In addition to a mixed acid and caustic stream, a pure sulfuric acid stream is produced, thus maintaining the sulfate balance in the system. This stream could be sent to a sulfuric acid plant for use as water makeup.

V

TEST PROGRAM OPERATING RESULTS

5.1 ABSORPTION—STRIPPING SECTION

The major results of the test program in the absorption-stripping section of the pilot plant operation were:

1. SO2 removal efficiencies of 90 to 95 percent were attained with inlet SO2 concentrations up to 3800 ppm. This was accomplished with two 10 foot absorption stages at 2000 lb/sq ft/hr gas flow and a pressure drop of 10 to 15 inches of water.

2. The process was operated at an average oxidation level of about 13 percent at an overall caustic utilization in the absorber of 80 percent or greater.

3. Maximizing the concentration of sodium bisulfite in the absorption tower minimizes oxidation and maximizes caustic utilization. It appeared that sodium sulfite was the oxidized species.

4. High sodium bisulfite concentrations were favored by lowered pH (approximately 5.0) and high inlet SO2 concentrations.

5. Gas rate and sodium sulfate concentration appeared to have little effect on oxidation.

6. Increased gas-liquid contact residence time in the tower increased oxidation. Oxidation is apparently controlled by the mass transfer of oxygen into the absorbing solution.

7. Stripper steam requirements (including preheat and losses) were close to 6 lb/lb of SO2 removed. This total included 4.25 lb steam/lb SO2 for preheat with the balance going to stripping and heat losses.

8. Closed loop operation was achieved except for sodium losses which were accounted for by mechanical leakage. Process liquor carryover in the towers can be controlled using demisters.

9. Heavy metal cation specifications for the cell feed liquor were obtained through appropriate treatment.

10. The operational problems with the pilot plant were mainly mechanical. Proper equipment and materials of construction selection will minimize operating difficulties in future plants.

5.2 ELECTROLYTIC CELL SECTION

The major results obtained in the electrolytic cell section of the pilot plant were:

1. The current efficiency for total caustic production by the "A" and "B" cells combined averaged 90-91% except when crystallization occurred in the cells. The high efficiency exceeds the design basis by 5-6 percentage points.

2. The maximum sodium sulfate feed concentration should be 3.5 N Na_2SO_4. Above this level, crystallization of the catholyte inside the cells occurs damaging the cells.

3. Overall "A" cell current efficiency averaged 90-93% (except when crystallization occurred in the cells), exceeding the design basis by 5-8 percentage points.

4. Overall "B" cell current efficiency averaged 96% in three measurements free of external and internal leakage. The current efficiency for purged H_2SO_4 ("B" anolyte) averaged 45%, exceeding the design basis by five percentage points.

5. Current efficiency appears to be independent of current density, at least in the range covered (i.e., 70% to 100% of design point).

6. The overall energy consumption per pound of caustic produced in the pilot plant was less than or equal to the performance objectives at each production level, except when crystallization occurred in the cells. The measured energy factors "bettered" the performance objectives by as much as 9% at the 100% production level.

7. Reduction of dissolved iron in the sodium sulfate cell feed stream to less than 0.1 mg/l was achieved using hydrogen peroxide to oxidize the ferrous ion to ferric before filtration.

8. Cell system availability during the last nine months of the twelve-month test program was over 90%. Cell maintenance time during the nine months was 408 hours.

9. Substantial reductions in cell voltage and, consequently, energy consumption were realized when lead alloy anodes were replaced with "inert" anodes. Reductions can reach over 25% at the higher current densities.

5.3 OVERALL CONCLUSIONS

The process is technically feasible with proper materials of construction and equipment. The features of no secondary waste disposal other than dilute sulfuric acid and on-site chemical regeneration are advantages, and the sulfur dioxide is recoverable as a product.

VI
DISCUSSION OF PROCESS RESULTS

6.1 ABSORPTION

The absorption of SO2 in caustic soda follows the reaction sequence:

$$2NaOH + CO_2 \longrightarrow Na_2CO_3 + H_2O \quad (1)$$
$$Na_2CO_3 + SO_2 \longrightarrow Na_2SO_3 + CO_2 \quad (2)$$
$$2Na_2CO_3 + SO_2 + H_2O \longrightarrow 2NaHCO_3 + Na_2SO_3 \quad (2a)$$
$$NaHCO_3 + SO_2 \longrightarrow NaHSO_3 + CO_2 \quad (2b)$$
$$Na_2SO_3 + SO_2 + H_2O \longrightarrow 2NaHSO_3 \quad (3)$$

In order to minimize the caustic required for a given SO2 removal, a high sodium bisulfite to sodium sulfite ratio is required. This ratio (S/C) is conveniently expressed as the ratio of total dissolved SO2 to total sodium as sulfite and bisulfite (all expressed in gm-ions/liter). This concept was first used by Johnstone, *et al.*, (9) in correlating SO2 vapor pressure over sodium sulfite–sodium bisulfite solutions. Operating S/C ratios for the absorber liquid effluent varied from 0.85 to 0.95 during the test program.

The absorption tower contained a quench section for flue gas cooling and fly ash removal and three packed absorption sections. Each packed section contained ten feet of two inch Tellerettes. The two lower packed stages were used as absorbing stages and the upper stage as a demister. This avoided the high liquid carry-over experienced during the initial shakedown runs when all three stages were used as absorbing stages.

6.1.1 SO2 Removal

With two absorption stages in operation, 90 to 95 percent SO2 removal was achieved with inlet SO2 concentration as high as 3800 ppm. These data are presented in Table F-2 in Appendix F. The system had enough capacity at the higher SO2 inlet concentrations to handle normal fluctuations in the inlet concentration. The absorber was never overloaded during the test program.

6.1.2 Mass Transfer Coefficients

Whitney, Hans, and Davis(8) measured mass transfer coefficients for the absorption of SO2 into caustic media. They found that for very alkaline systems the gas phase resistance was controlling. However, as the absorption increased and sulfite and bisulfite became the predominant species, the liquid phase resistance became limiting. This conclusion was based on lower overall gas phase mass transfer coefficients as conversion increased.

Johnstone and Singh(11) studied the absorption of SO2 in alkaline media and found the mass transfer coefficients varied with the gas rate raised to the 0.8 power. Their system however was more dilute and more alkaline than concentrations studied in the present work. Hein, Phillips, and Young(10) found that gas rate had no effect on the absorption of SO2 with ammonia solutions. The pH of their absorbing liquor varied from 5.6 to 6.8, indicative of high ammonium bisulfite concentrations.

For the magnesium sulfite-bisulfite-sulfate system, Pinaev (7) found that the presence of the sulfate increased the sulfur dioxide vapor pressure at a given bisulfite-sulfite concentration.

It was found that S/C ratios in the draw liquor of 0.90 and above could be easily obtained at concentrations of sodium sulfate up to 24 percent (wt). This verified the Johnstone vapor pressure data. Thus, it can be concluded that sodium sulfate does not affect the SO2 vapor pressure for the sodium system at concentrations up to 24 percent (wt).

Mass transfer coefficients were calculated for the present system using interstage data collected during the program.

The equilibrium SO2 concentration in the gas phase was found using the vapor pressure data of Johnstone, et al. (9) Overall gas phase mass transfer coefficients were calculated for both the top and bottom stages and are presented in terms of height of a transfer unit (Hog) using a packing height of 10 ft per stage. The results are summarized in Table F-3 in Appendix F.

The absorption was found to be limited by the S/C ratio of the absorbing liquor. Below an S/C ratio of 0.925, Hog is constant at 3.5 ft. However when the S/C ratio reaches 0.925, Hog rises dramatically. This is shown in Figure 6.1.

At S/C ratios much above 0.90, the SO2 vapor pressure curve increases rapidly. In calculating the number of gas phase transfer units for each packing stage, it was assumed that operating and equilibrium lines were straight. For stage 2, this gave conservative answers since the S/C ratio of the interstage liquor was usually 0.85 or less. The vapor pressure of SO2 starts to become significant at S/C of 0.80 and above.

For stage 1, the assumption of a straight equilibrium line is not as appropriate because of vapor pressure nonlinearity. Also, experimental accuracy for measuring inlet SO2 concentration and liquid phase compositions in this region was such that small errors caused a large variation in the calculation of Hog. This factor is

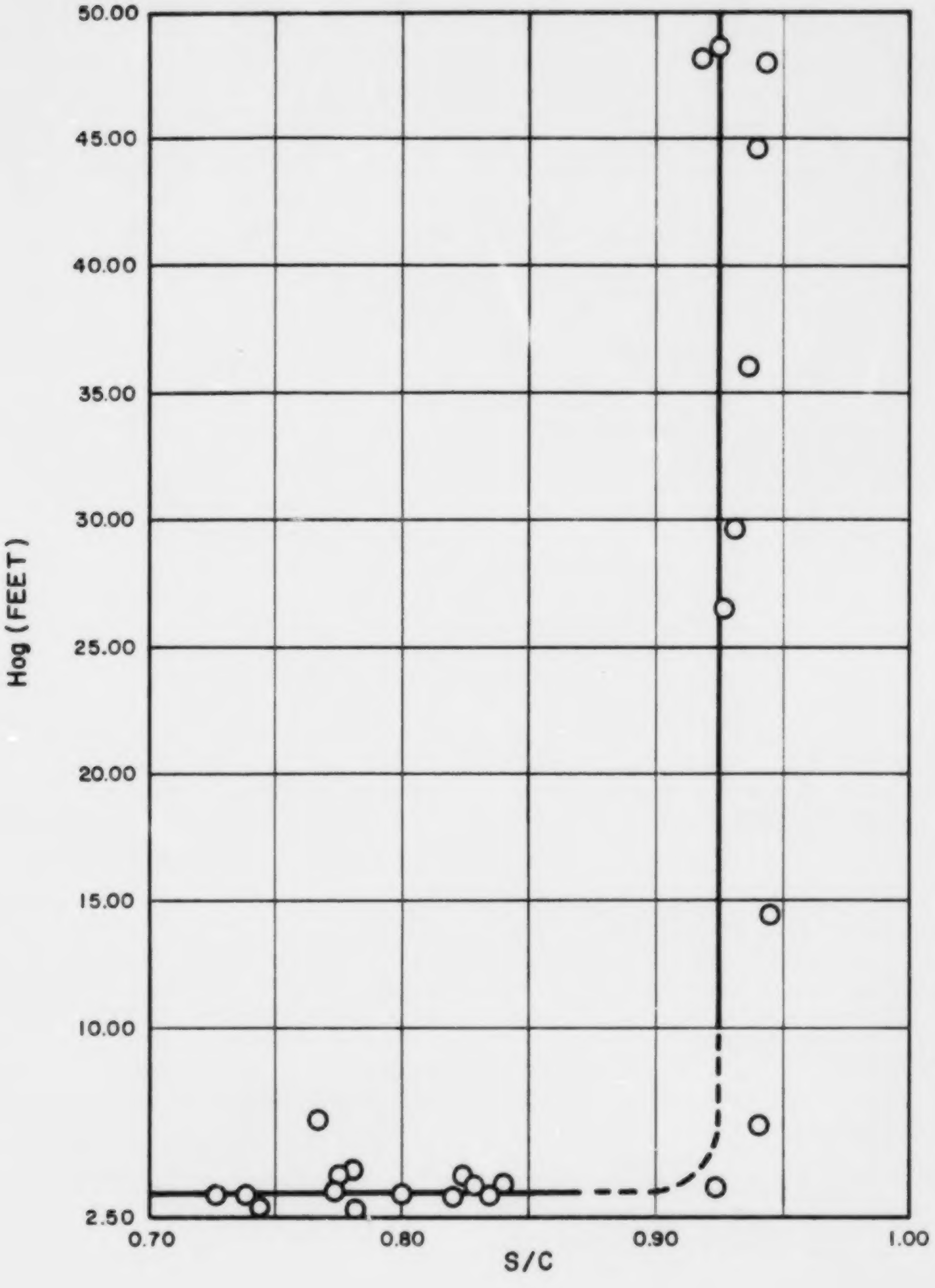


FIGURE 6.1 HEIGHT OF A TRANSFER UNIT, Hog VS. S/C

probably responsible in large measure for the almost vertical rise.

Figure 6.2 presents the overall gas phase mass transfer coefficient (Kga) as a function of superficial gas velocity (Gm). The data points shown are only those where the S/C ratio is below 0.90. The overall gas phase mass transfer coefficient is proportional to G 0.84. This is consistent with the data of Johnstone and Singh(11) for the absorption of sulfur dioxide in alkaline solutions. At low levels of SO2 removal (60 to 70 percent), the mass transfer coefficient was proportional to G 0.8. In view of the errors involved in measurement and the assumption of straight line equilibrium, this agreement is quite good. Insufficient data were taken to determine the controlling resistance. However, at low SO2 removals, the gas phase resistance appears to predominate. The gas phase contribution will decrease as conversion increases as a result of the increased SO2 vapor pressure above the solution. Thus, the overall transfer coefficient is determined by gas phase or liquid phase resistances dependent upon the region of operating conditions.

In the majority of the test runs, the bottom stage was ineffective for SO2 absorption.* Furthermore, as shown in Table F-2, it contributed very little to the overall oxidation. However, the bottom stage did increase overall sodium utilization by increasing the S/C ratio. An increase in the S/C ratio from 0.80 to 0.90 at 10 percent oxidation decreased caustic requirements by approximately 9 percent for a given SO2 removal. This is very significant to the overall process economics as 90 percent removal could not be achieved in a one stage operation with recirculation. The packing height in this stage was not varied during the test program but results indicate that a lower height would have been as effective.

6.1.3 Caustic Utilization

Caustic utilization can be defined as "the ratio of the theoretical minimum caustic required for a given SO2 removal to that actually used." Process limitations that increase the requirements above the theoretical minimum are oxidation, pH adjustment required in feed liquor preparation, and completeness of the absorption reaction (S/C ratio).

The theoretical minimum caustic requirement is defined as the stoichiometric equivalent of the SO2 removed from the gas. This assumes that:

1. No oxidation occurs,
2. No pH adjustment of feed liquor is required, and
3. All SO2 is absorbed as bisulfite.

*See Table F-2, Appendix F.

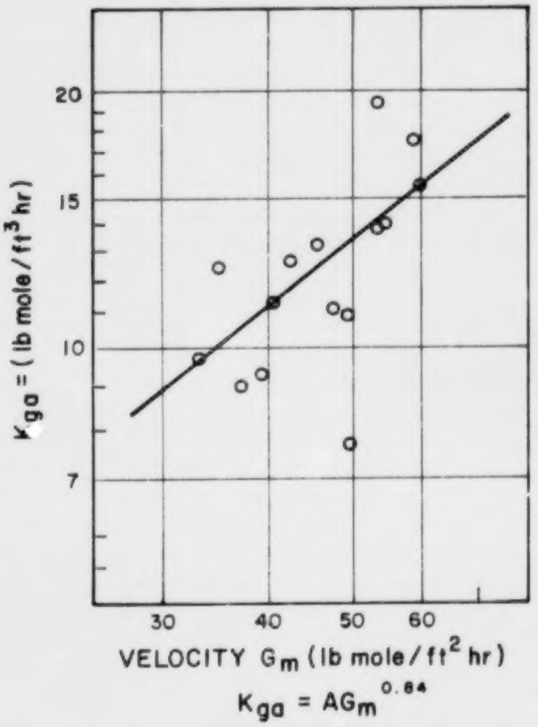


FIGURE 6.2 OVERALL GAS PHASE MASS TRANSFER COEFFICIENT VS. SUPERFICIAL GAS VELOCITY

The first assumption is obvious, for any oxidation will require 2 moles of caustic per mole of sulfur. The second assumes stoichiometric acid addition to the net draw liquor from the absorber and 100 percent effectiveness in releasing the SO2. This is not the case as will be seen in Section 6.3. The minimum recycle caustic required was 3.2 percent of the caustic feed to the absorber. This is based upon the measured stripping effectiveness of the pilot plant tower. With more stages the required amount of recycle could be reduced. The third assumption disregards SO2 vapor pressure over the absorbing liquor. At the absorption temperature encountered in the pilot plant (120 F), the limiting S/C ratio according to the Johnstone data is about 0.925. This fact is verified by the rapid increase in the height of a theoretical transfer unit at a S/C ratio of 0.925. Thus, the minimum caustic requirement is not equal to the SO2 removed but is 11.3 percent greater than the SO2 removed. This corresponds to a caustic utilization of 0.898. The base value of 1.0 was chosen because the caustic requirement for a given SO2 removal is the parameter of interest.

It is important to realize that overall caustic utilization is a function of all the factors mentioned and not just the level of oxidation. If one assumes a base case, as shown on Table F-1 in Appendix F, caustic utilization in the absorber is 83 percent. Furthermore, decreasing the S/C ratio from 0.90 to 0.85 will increase caustic consumption by 4.9 percent, and increasing the amount of oxidation from 10.0 to 15.0 percent will increase caustic consumption by 3.7 percent. Additionally, incomplete stripping of SO2 from neutralized cell feed liquor will increase the caustic consumption. A five percent excess recycle acid flow will increase caustic consumption by 4.2 percent and 1000 mg/l of residual SO2 in the stripper bottoms will increase caustic consumption by 1.9 percent.

Caustic utilization averaged about 0.78 for the test program. This can be translated into an oxidation of approximately 13 percent, an S/C ratio of 0.925 and a caustic recycle of five percent.

6.1.4 Entrainment

During the early part of the test program, significant chemical losses were experienced. These losses were attributed to the entrainment of process liquor overhead from the absorption tower. Considerable dilution also occurred as a result of quench water carry-over into the bottom stage. In addition to the penalizing effects of the dilution, the high calcium and magnesium content of the entrained quench water was detrimental to the performance and operation of the cell system.

The process fluid entrainment loss was traced to the recirculation liquor feed distribution nozzles. These were high-pressure drop Bete nozzles which produced a fine atomizing spray. Figures 6.3 and 6.4 present process fluid entrainment as a function of gas rate and liquid recirculation rate, respectively. The combination of high gas velocities through the chimney trays and the atomized spray produced by the Bete nozzles was responsible for the entrainment. When these nozzles were replaced with a splash plate type distributor, the entrainment dropped drastically.

The top packed section was also used as a demisting section to further limit process losses. The third stage of Tellerettes was not effective for removing the condensed water caused by cooling of the flue gas. This water loss was due to the humidity profile of the flue gas across the tower and cannot be attributable to inefficient demisting by the Tellerettes. All overhead chemical losses were eliminated using the above-mentioned modifications.

Figures 6.5 and 6.6 show the entrainment from the quench section as a function of gas rate and impingement tray water flow, respectively.

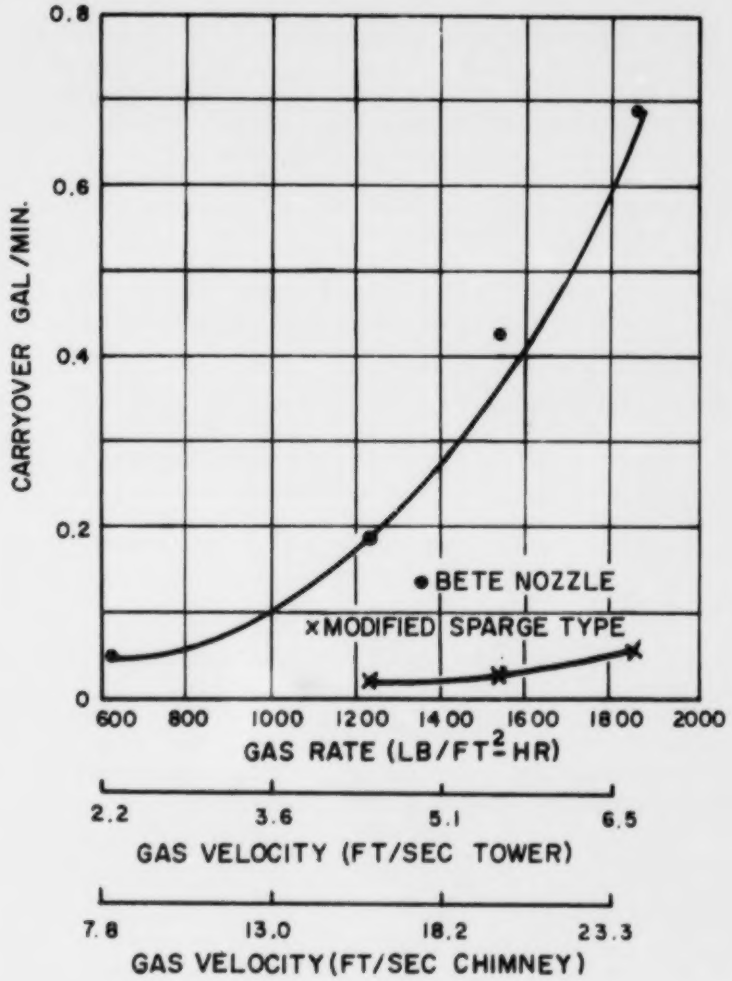
With no demister present, carry-over was large over the range of gas rates and plate water rates studied. Apparently, the high gas velocities through the chimney trays were responsible for the entrainment. A polypropylene demister pad was installed between the quench section and the bottom stage. This eliminated carry-over below gas rates of 1700 lb/hr/ft²; measured values were in milliliters of water per hour.

Due to tower geometry, the demister had to be installed with an insufficient clearance between the pad and the bottom chimney tray. Therefore, as the gas rate was increased, the effective area of the pad was reduced as the gas passed through the smaller chimney tray. This resulted in demister flooding at gas rates above 1700 lb/hr/ft².

6.1.5 Pressure Drop

Figure 6.7 shows the pressure drop through the entire absorption tower, including quench section, as a function of gas rate. The tower internals account for most of the drop since the unit was operating below flooding conditions when the highest pressure drops were measured.

The relative contributions of tower internals and circulating liquor to the pressure drop can be found by examining a specific case. The pressure drop for a typical run was 7.6 in. of water for the entire tower including the



LIQUID RECIRCULATION CONSTANT $\begin{cases} = 15 \text{ GPM BETE NOZZLE} \\ = 25 \text{ GPM SPARGE NOZZLE} \end{cases}$

FIGURE 6.3 ENTRAINMENT FROM
STAGE I AS A FUNCTION OF GAS RATE

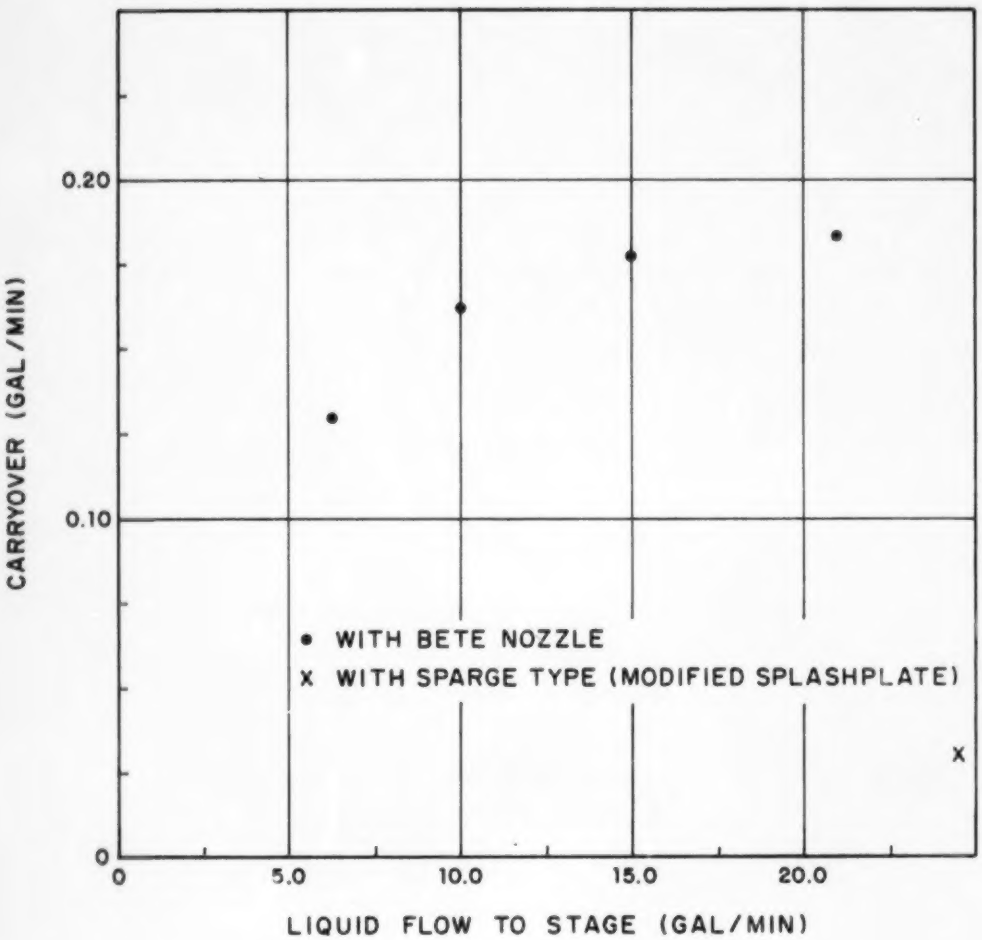


FIGURE 6.4 ENTRAINMENT FROM STAGE 1 AS A FUNCTION OF LIQUID RECIRCULATION RATE-GAS RATE CONSTANT @ 1200 LB / FT^2 HR.

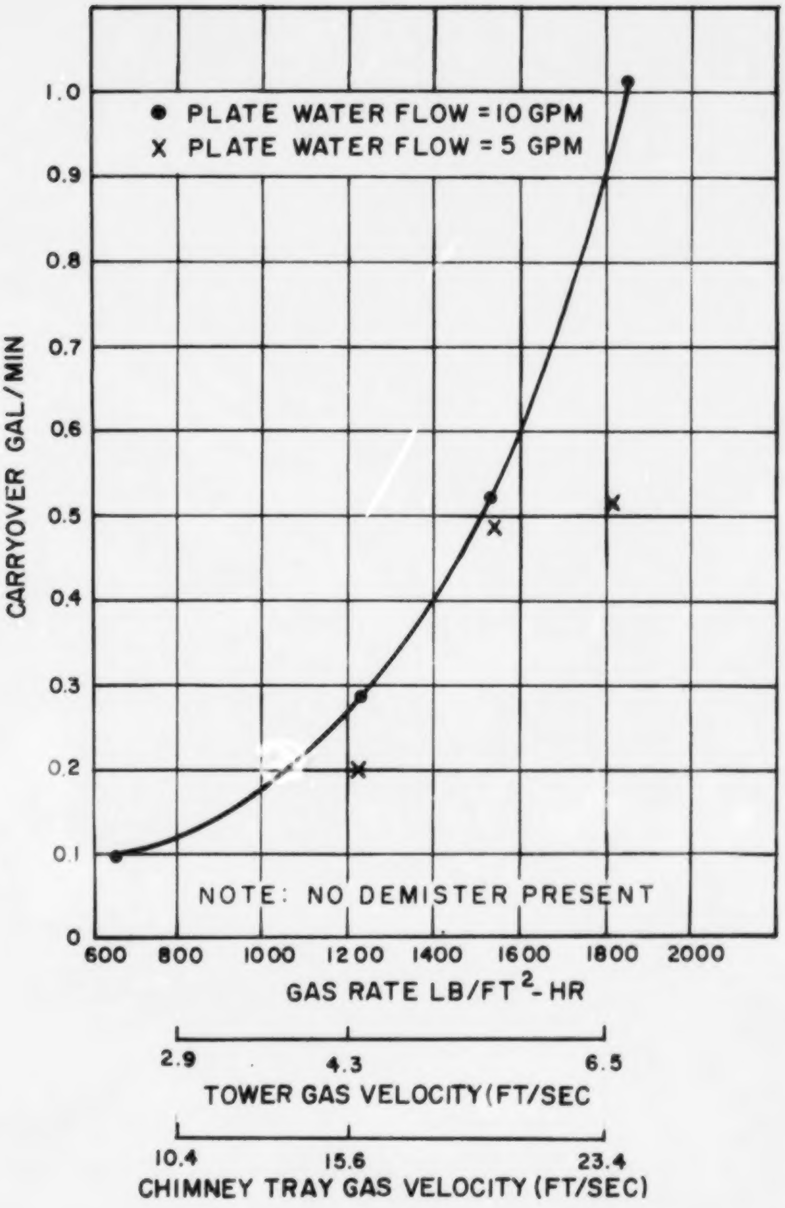


FIGURE 6.5 ENTRAINMENT FROM QUENCH SECTION AS A FUNCTION OF GAS RATE-BAFFLE FLOW CONSTANT

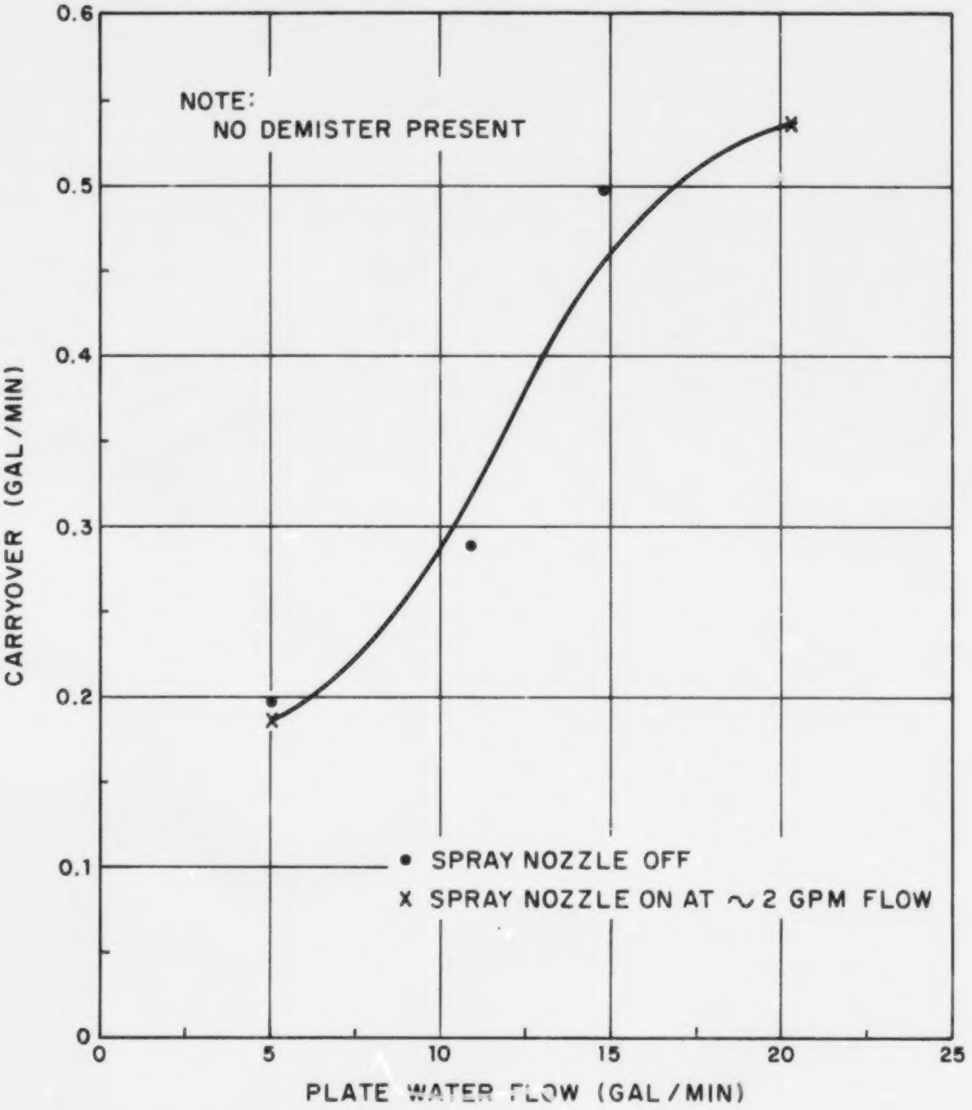


FIGURE 6.6 ENTRAINMENT FROM QUENCH SECTION AS A FUNCTION OF PLATE WATER FLOW- GAS RATE CONSTANT @ 1200 lb/ft^2 hr

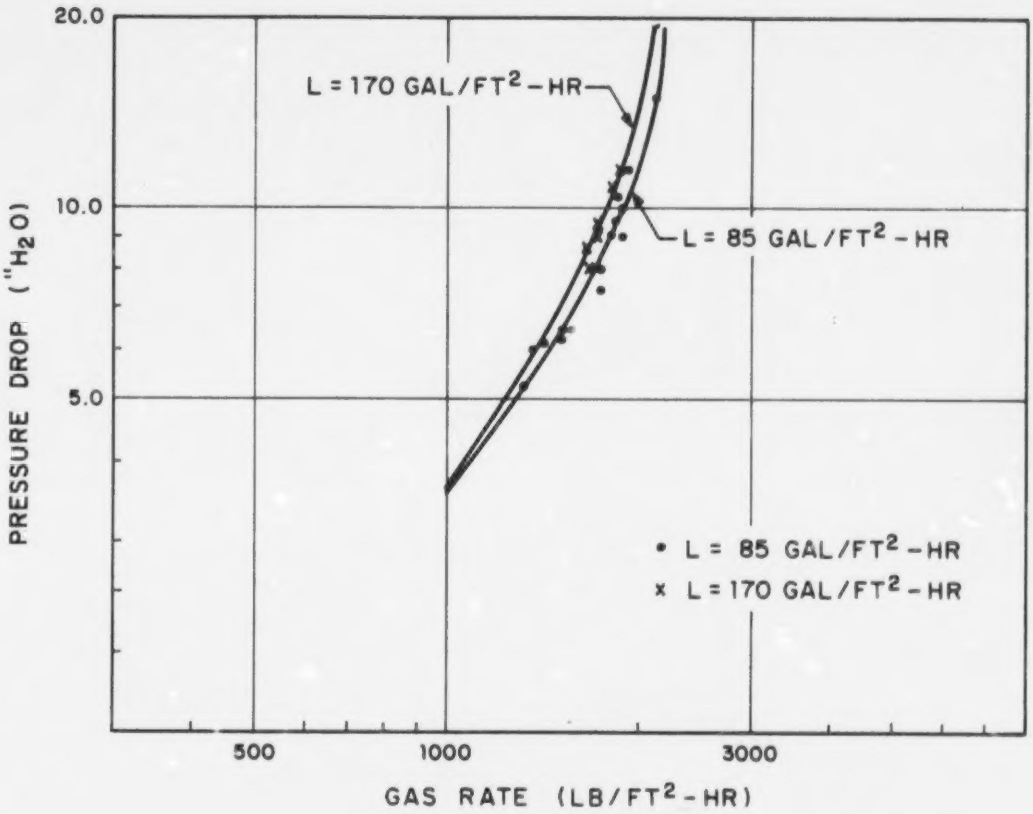


FIGURE 6.7 PRESSURE DROP THROUGH ABSORPTION TOWER (Including Quench Section)

quench section and demister. The drop across the top stage including chimney tray (used as a demister and hence essentially dry) was 1.9 in. of water. Thus, the drop across the three packed stages was 5.7 in. of water or 75 percent of the total. The operating pressure drop across the impingement tray and demister was 1.6 in. of water or 21 percent of the total drop. The circulating liquor, therefore, contributed only 0.3 in. of water (4 percent) to the pressure drop across the tower. This level is well below flooding conditions.

6.1.6 Particulate Removal, NOx and SO3

During the latter part of the test program, EPA performed a series of measurements to determine the amount of particulates, NOx and SO3, at the absorption tower inlet and their removal from the flue gas. The removal results were inconclusive, but the absolute level of these components was reasonably established.

The measured outlet concentrations for all three variables were greater than the inlet concentrations. The inlet and outlet measurements were taken on different days and at different times of day, so varying boiler load conditions may account for some discrepancy. Table 6.1 presents the EPA results.

NOx levels were also measured using the WEPCO "theta" sensor. Both inlet and outlet concentrations were measured for constant boiler load conditions. The NOx levels by this analysis were reduced from 385 ppm to 231 ppm in the absorption tower. The indicated removal is consistent with published data on NOx removal by caustic scrubbing systems.

TABLE 6.1
PARTICULATES NOx AND SO3 LEVELS ON ABSORBER INLET AND OUTLET (MEASUREMENTS BY EPA EXCEPT AS NOTED)

	Inlet	Outlet
Total Particulates (gr/SCF)	0.006-0.007	0.04 ± 0.014
Particulates as Sulfate (gr/SCF)		0.004
SO3 (ppm)	9 - 29	30 - 100
NOx (ppm)	134/220	329/287
	167/145	375/417
	385*	231*
Water (% moisture)		7.0

1. No oxidation occurs,
2. No pH adjustment of feed liquor is required, and
3. All SO2 is absorbed as bisulfite.

*Measurements by WEPCO "theta" sensor

6.2 OXIDATION

Oxidation was defined as the amount of SO2 removed that appears as sulfate in the adsorber net draw. It is expressed as percent of SO2 removed. The determination of the amount of oxidation that occurred in the absorber and of those parameters affecting oxidation was a primary goal of the test program. Increased oxidation directly affects power and capital costs by increasing the number of "B" cells relative to "A" cells as well as increasing the total caustic required for SO2 removal. Furthermore, the quantity of SO2 product will be reduced with increased oxidation. Thus, operation with a minimum amount of oxidation is the most economical for a given sodium sulfite-sodium bisulfite ratio in the absorber.

Anitoxidants were considered as a possible means of minimizing oxidation in the absorber. It is necessary, of course, that any antioxidant used must not adversely affect the performance of the electrolytic cells. Therefore, the effect of several candidate phenolic-based antioxidants was studied using small, bench-scale, Type "A" cells. All four candidates tested (hydroquinone, para-aminophenol, paraphenylene diamine and catechol) resulted in fouling of the cells from decomposition products. No further testing was performed.

6.2.1 Literature Survey

There is very little data available in the literature on the oxidation of a mixed sodium sulfite-bisulfite salt solution. However, several authors (1,2,3,4) have published information on sulfite oxidation relating to the calibration of biochemical reactor systems. Sulfite oxidation is used for measuring oxygen absorption into the liquid phase.

Fuller and Crist(1) found that the oxidation of sodium sulfite is first order with respect to sulfite concentration below a concentration of 0.015 mole per liter. Above this concentration the reaction is limited by oxygen transfer into the liquid phase and is independent of sulfite concentration. They also noted a marked catalytic effect by heavy metals such as copper at concentration levels as low as 10^{-8} moles per liter. The amount of oxygen absorption was decreased by the addition of acid to the system. Acid addition will convert the sulfite to bisulfite. Since oxygen absorption was used as a measure of oxidation, Fuller and Crist report that bisulfite solutions are not oxidizable and the decrease in oxygen absorption is dependent only on the sulfite ion present. The rate of oxygen absorption, however, does not change, absorption terminating upon the reaction of all available sulfite.

Srivastava, et al.(2) confirm the Fuller and Crist results by reporting the oxidation of sodium sulfite is zero order with respect to sulfite concentrations above 0.04 moles/liter and first order with respect to oxygen concentration. They also noted a catalytic effect of cobalt addition at levels of 30 to 40 ppm. Similar results are reported by Phillips and Johnson(5), and Yagi and Inove(3).

Chertkov(4) studied the oxidation of magnesium-sulfite-bisulfite sulfate solutions. He noted that in dilute solutions (less than 12-wt percent salts) the absorbed SO2 is almost completely oxidized. A lower oxidation was observed in solutions with magnesium sulfate concentrations above 12 percent. Lowered oxidation was attributed to an increased liquid phase transfer resistance for oxygen absorption resulting from the increased liquid viscosity and density. Oxidation was found to be greater at a lower pH, contrary to the Fuller and Crist results. This apparent discrepancy can be explained if one examines the study by Potts, _et_ _al_.(6). Using a proposed free radical mechanism for sulfite oxidation and the derived rate expression as follows:

$$\frac{d(SO3^{=})}{dt} = \frac{q(H303^{-})}{\sqrt{H^{+}}}$$

Potts, _et_ _al_, calculated the hydrogen and bisulfite ion activities for a calcium salt system. The ratio (HSO3-) H+ was shown to increase or decrease with pH depending upon whether or not the system is saturated with CaSO3 1/2H20. Decreasing pH inhibited oxidation for unsaturated solutions and the opposite was true for saturated solutions. Chertkov also noted the effect of gas rate on oxidation. As the gas rate was decreased over a considerable range, the amount of oxidation decreased. No explanation was offered for this occurrence.

In general, the extent of oxidation should be influenced by the concentration of oxygen in the flue gas, the characteristics of the absorbing liquor, and the design of the absorption tower (incorporating such variables as gas rate, gas-liquor contact time, and type and volume of packing). This test program studied the effect of operating variables only. These included the characteristics of the absorbing liquor and gas and liquid rates within the tower. Oxygen concentration, packing volume and physical system characteristics were not studied.

6.2.2 Data Reduction

During a test run, samples of caustic feed to the absorber, interstage circulating liquor, and absorber net draw were taken and analyzed for sodium sulfite, bisulfite, bicarbonate and sulfate. Caustic flow rate, gas flow rate, and SO2 inlet and outlet concentrations were monitored continually and averaged hourly. Material balances around the absorber were used to determine the reliability of each data point. Typically, there were five data points generated per day for a three to five day run at specified conditions.

The SO2 disappearance from the gas stream was calculated from the outlet gas flow rate and inlet and outlet SO2 concentrations. Gas flow measurements, based on the pressure drop over a straight run of pipe, calibrated using a standard pitot tube, could be determined to ±360 pounds per hour (2 percent of full scale). SO2 concentrations, determined using an Intertech analyzer calibrated by a standard span gas, could be determined to ±50 ppm. This would result in an error of ±0.3 gm-mole/hr, or less than one percent of the average removal. Inlet and outlet SO2 levels were measured as dry gas eliminating any variances due to water content. SO2 measurements agreed quite well with those determined by EPA using wet chemical analysis (see Section 8).

The SO2 appearance in the liquid stream was also determined. The total sodium fed to the absorber was determined from the caustic flow rate and the chemical analysis. Free sodium was determined by titration with hydrochloric acid and sodium sulfate was determined gravimetrically by barium chloride precipitation. The total sodium determination was accurate to ±5 percent and the caustic flow rate to approximately 2 percent. Measurements of the total sodium leaving the absorber and the total liquid phase sulfur appearance were hindered by the lack of a reliable flowmeter on the net draw.

A total sodium balance agreeing to within 15 percent was used as one criteria for data reliability. Based upon the system water balance, some concentration of the process liquor is expected (See Section 6.5). However, the absorber net draw should have shown no more than a 15 percent concentration. Total sodium analyses for the net draw and caustic feed were compared directly (assuming equal mass flow rates) and a data point was eliminated if the ratio deviated by more than 15 percent. This ratio also includes analytical errors which could be isolated from the concentration effect. The net draw flow rate was calculated by assuming a sodium balance across the absorber.

The total liquid phase sulfur appearance was calculated by two methods, one being a slight variation of the other. In the first method, sulfur as SO2 was found from the sodium sulfite and bisulfite concentrations and the calculated net draw flow rate. The sulfur as sodium sulfate was determined by the difference between the inlet free sodium and sodium as sulfate-bisulfite and bicarbonate analyzed in the draw stream.

In the second method, the sulfur appearance as SO2 was calculated as above. However, sulfur as sodium sulfate was found from the difference between caustic and net draw sulfate analyses. Liquid phase sulfur appearance to within 10 percent of gas phase sulfur disappearance was used as the second criteria of data reliability. Sample calculations have been presented in Appendix C.

Oxidation was primarily calculated by two methods. A sodium balance method was based on sodium and sulfur material balances. Sulfur appearance as sodium sulfate (determined by sodium difference as above) was compared to the total liquid phase sulfur appearance (sodium sulfite, bisulfite, and sulfate). This method is subject to the errors in absolute chemical analysis and net draw flow rate mentioned above. A ratio method compares the total sodium to sulfate ratios of the caustic and net draw streams. Given an analytically determined S/C ratio, there is only one oxidation level that can satify both the sodium to sulfate ratio and the inlet caustic conditions. This method is independent of SO2 removed and net draw flow rate and has, therefore, been used in all the data correlation.

A third method, used only as a check, is based on the acid flow to the stripper. Given the acid molar flow rate to the stripper and the molar flow rate of caustic required to neutralize excess acid in the pH buffering system, one can calculate the amount of SO2 released. Since SO2 absorbed as sodium sulfate will not be released, the gas phase disappearance of SO2 through the absorber will be greater than the amount of SO2 released in the stripper. The difference is the amount of oxidation that occurred in the absorber. However, due to the unreliability of the acid flow meter and the batch-wise measurement of buffering caustic requirements, this method was applied for conditions averaged over a whole run and has a very low confidence level. Examples of these calculation methods are presented in Appendix C.

The data correlations presented in the following section are based upon a least squares analysis of all the 100 plus acceptable data points (or 16 acceptable points for interstage data.) The variance about the straight line was calculated and a band of one standard deviation (J) has been shown on all plots. The actual data points shown on the graphs are individual run averages and are used as representative of all the data points.

The wide scatter in the data is probably a result of several factors. The imprecision of the gravimetric sulfate analysis (see Section 8), variations in SO2 inlet concentrations due to boiler load changes, normal process fluctuations, and instrumentation errors all contributed to the scatter. The samples used were spot samples and no attempt was made to obtain averaged ones. In view of the magnitude of other errors and fluctuations involved, such an attempt would result in a negligible increase in overall accurancy.

6.2.3 Results

Table F-1 in Appendix F summarizes the oxidation results of the pilot plant operation. The data are composed of 22 runs based on varying operating conditions. Run 1 to run 6 were initial shakedown runs and have significant material balance errors. They were therefore omitted from the final tabulation. Runs 8,9,16, 17, 19, and 33 were omitted due to material balance errors, significant process dilution, or unsteady state operation. The results cover SO2 inlet gas concentrations from 1000 to 3700 ppm, gas rates from 4500 to 8700 lb/hr (4-7 FPS), and cell feed liquor concentrations from 2.5 N to 4.0 N sodium sulfate. SO2 removal varied from 83 to 97 percent. Each run consists of three to fifteen distinct data points after screening for material balance reliability. The majority of those points contained absorber feed and net draw analyses only, however, several included interstage analyses for the determination of absorption and oxidation profiles. These runs are presented in Table F-2 in Appendix F.

The major results of pilot plant oxidation studies were:

1. Oxidation levels in the absorber varied from 7 to 25 percent with an average of 13.3 percent.

2. Oxidation decreased as the amount of SO2 removed increased from 125 to 300 gm-mole per hour.

3. The effect of the amount of SO2 removed (i.e. the combination of inlet SO2 concentration and gas rate) on oxidation can be related to increased sodium bisulfite concentrations. The higher the sodium bisulfite concentration, the lower the oxidation. Thus sodium sulfite is the oxidized species.

4. The most oxidation occurred in the top stage, the stage with the highest sodium sulfite concentration.

5. Oxidation is a function of the solution pH as determined by the concentrations of sodium sulfite and sodium bisulfite. At a given level of dissolved SO2, oxidation decreased as the sodium bisulfite concentration increased.

6. Oxidation decreased as the absorption profile shifted toward the top stage. As the fraction of the total SO2 removal in the top stage increased, the sodium bisulfite in the top

stage increased. This minimized the time that sodium sulfite existed in the tower.

7. Splitting the caustic flow between the top and bottom stages increased oxidation at constant S/C in the draw liquor by shifting the absorption profile toward the bottom stage.

8. Increasing the amount of heavy metals in the absorber feed increased oxidation. Low contaminant levels (less than 0.1 mg/l) can be achieved through proper materials of construction.

9. The sodium sulfate concentration in the circulating liquor had little effect on oxidation.

10. Increased gas-liquor residence time increased oxidation. Oxidation appears to be controlled by the liquid phase mass transfer resistance to oxygen absorption.

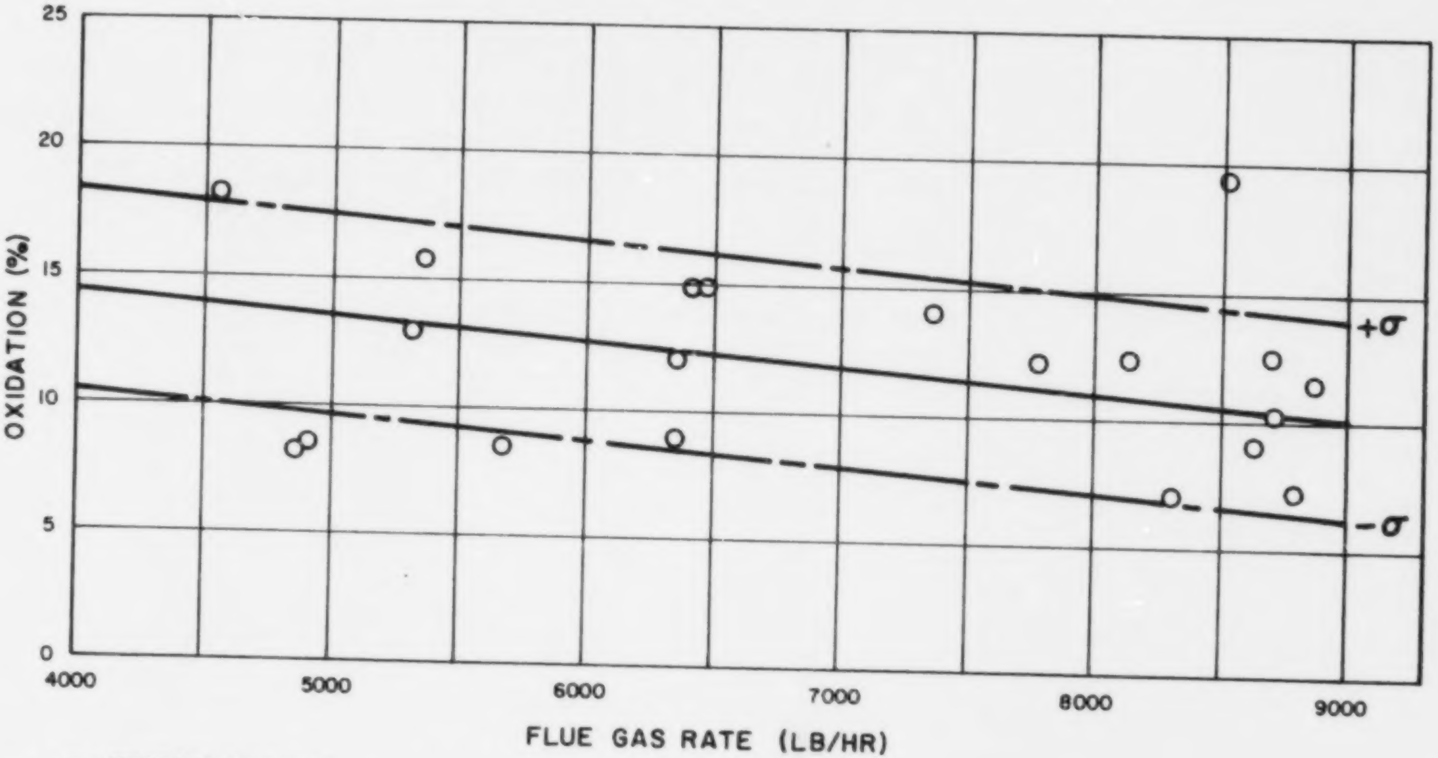
6.2.4 Discussion of Results

There were two primary goals for the pilot plant oxidation studies. The first was to define where oxidation was occurring, what species were being oxidized, and what chemical parameters affected the amount of oxidation. The second was to define the influence of operating parameters, such as gas rate, on oxidation and determine what operating region minimized oxidation.

The effect of gas rate on the amount of oxidation is shown in Figure 6.8. As the gas rate through the absorption tower was increased by a factor of two, oxidation decreased by approximately 30 percent. This finding is consistent with Chertkov's results for the magnesium salt system.

Figure 6.9 presents the effect of SO2 inlet concentration on oxidation. As the inlet concentration was increased by a factor of two, oxidation decreased by approximately 30 percent. The product of gas rate and SO2 inlet concentration, at a specific percent removal, is the total SO2 removed in the absorber. Figure 6.10 shows that as the removal increased by a factor of two, oxidation decreased by 50 percent. The amount of SO2 removal can be related to the system loading.

System loading can be defined as "the total amount of dissolved SO2 in the absorbing liquor." As the loading increases, for a constant caustic feed rate, the absorption reaction is driven more toward completion and sodium bisulfite becomes the predominant species. Figures 6.11 - 6.13 show the influence of gas rate, SO2 inlet



σ = STANDARD DEVIATION

FIGURE 6.8 THE EFFECT OF FLUE GAS FLOW ON OXIDATION (SO_2 INLET CONCENTRATION VARIED)

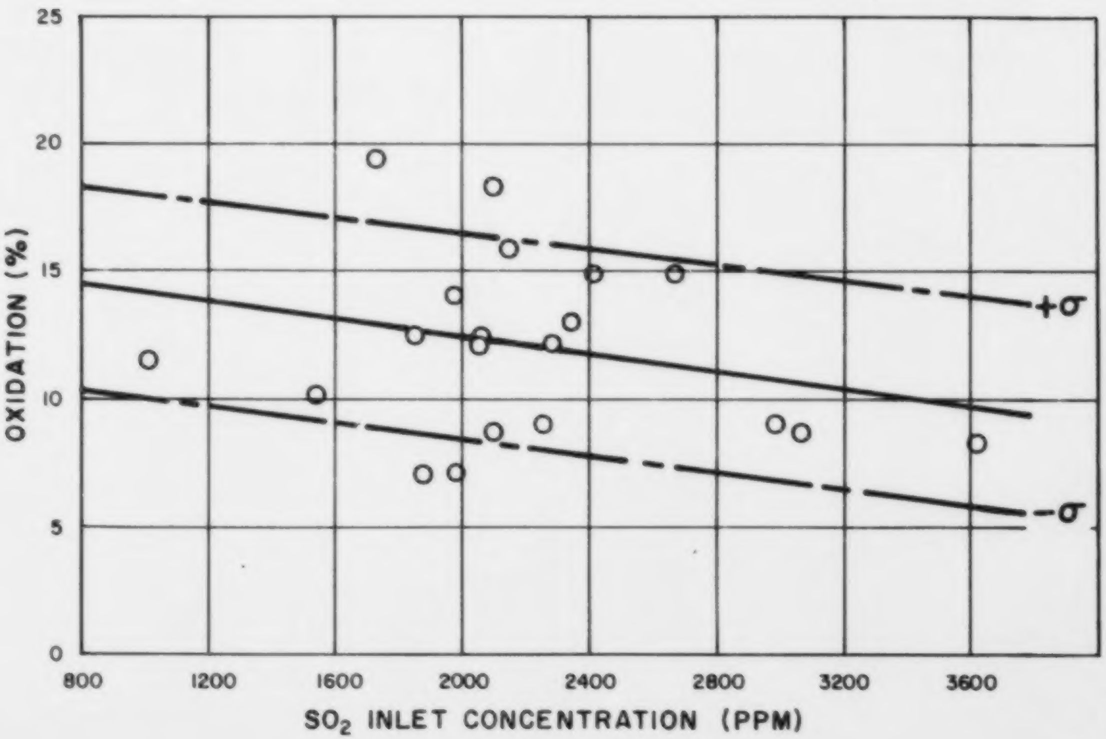


FIGURE 6.9 THE EFFECT OF SO_2 INLET CONCENTRATION ON OXIDATION (FLUE GAS FLOWRATE VARIED)

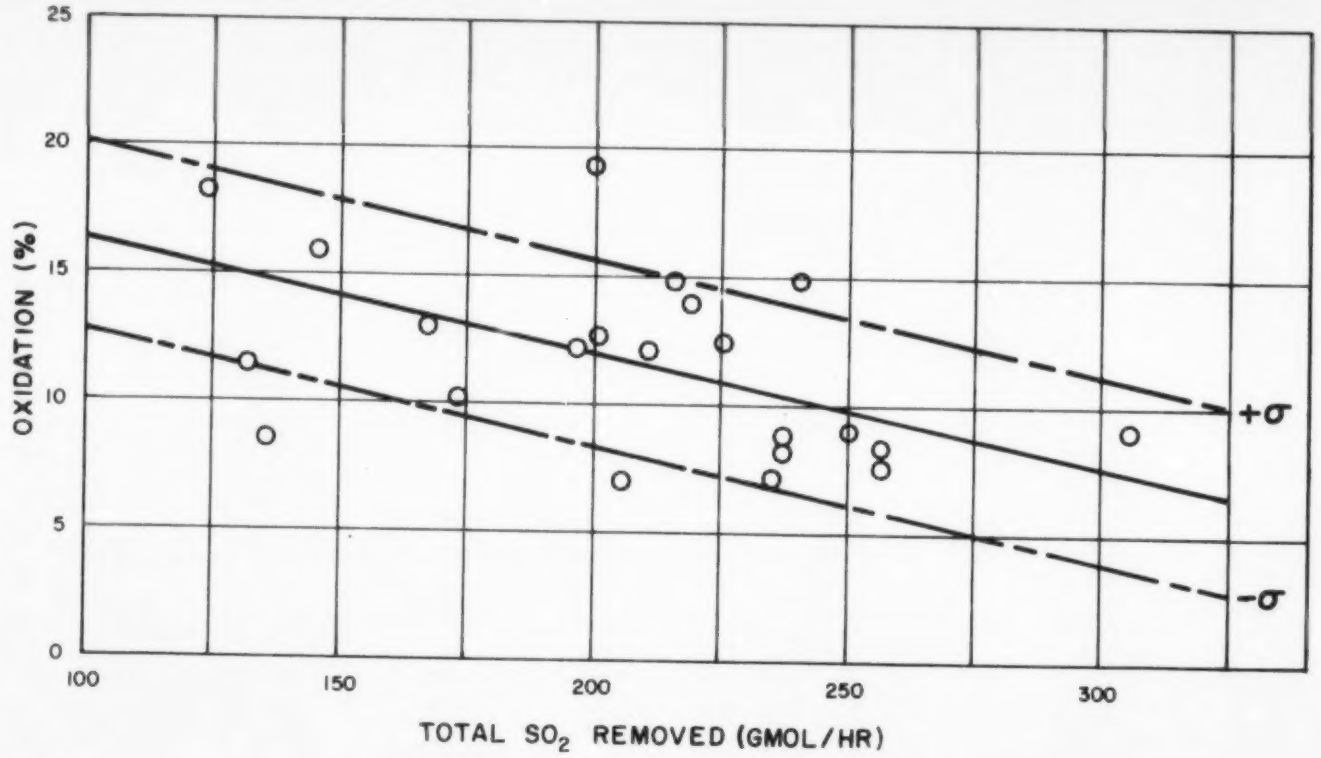


FIGURE 6.10 THE EFFECT OF TOTAL SO_2 REMOVED ON OXIDATION

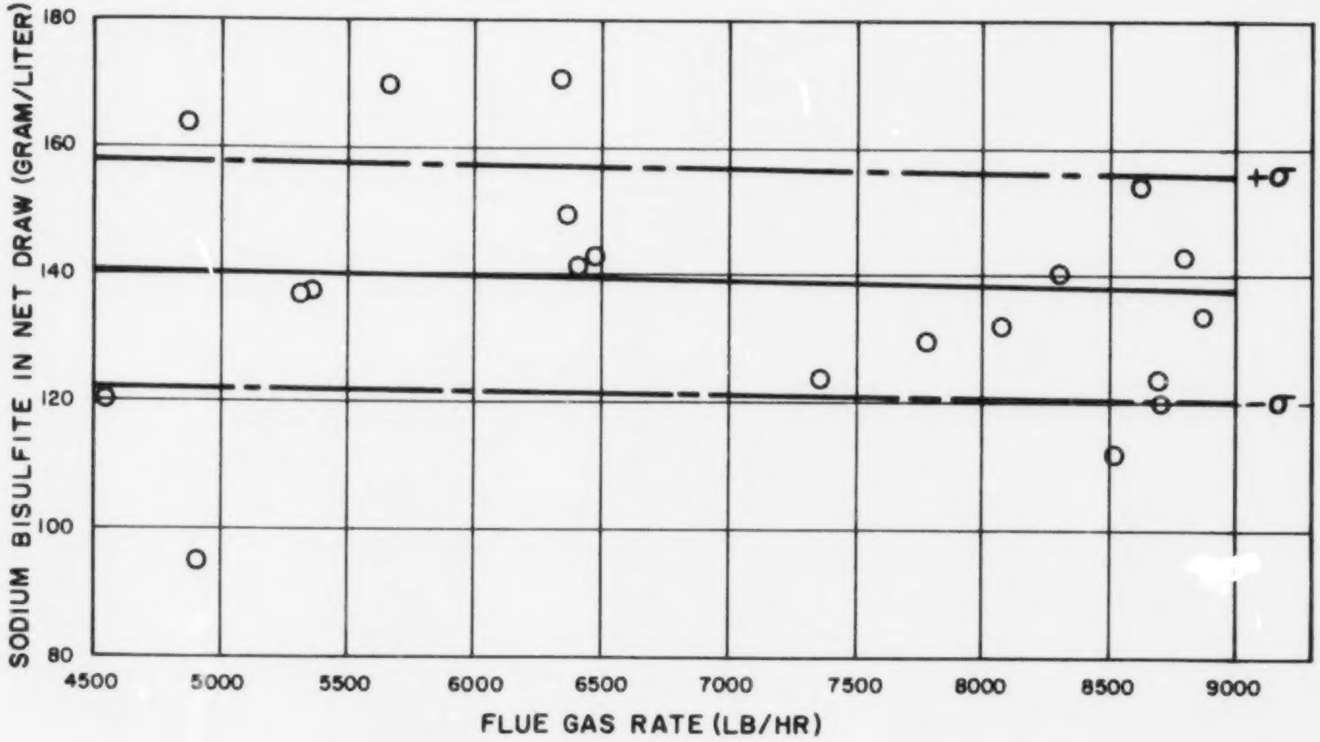


FIGURE 6.11 THE EFFECT OF FLUE GAS FLOWRATE ON THE NET DRAW SODIUM BISULFITE CONCENTRATION (SO_2 INLET CONCENTRATION VARIED)

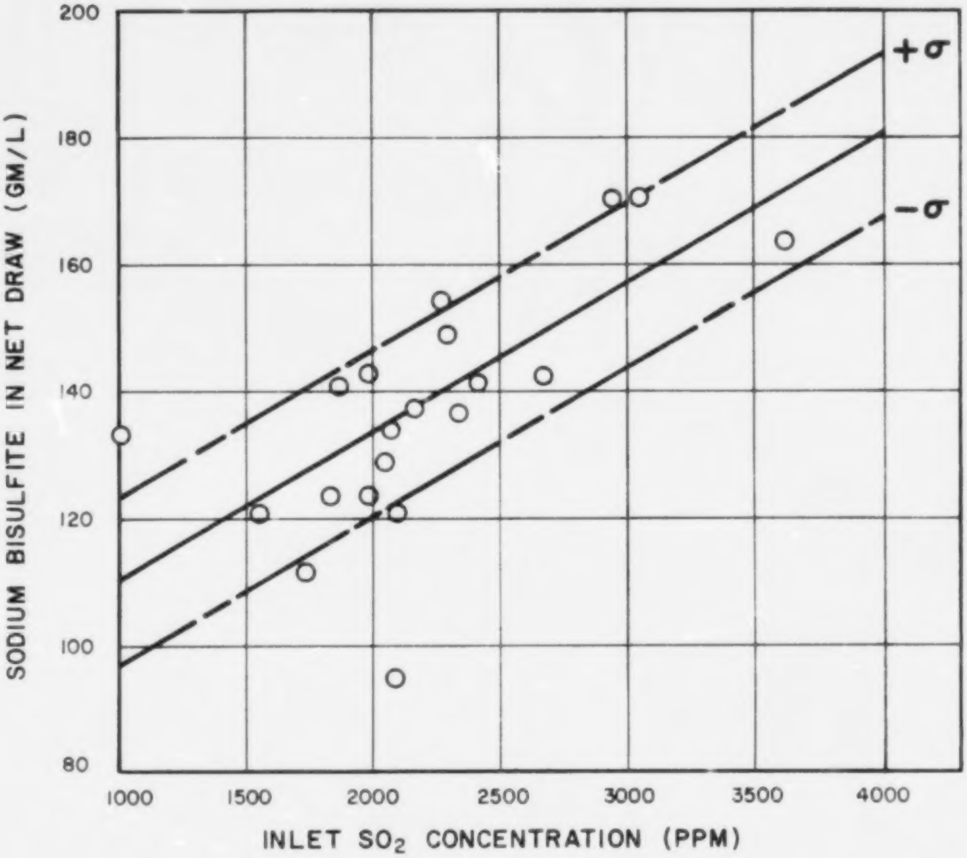


FIGURE 6.12 THE EFFECT OF SO_2 INLET CONCENTRATION ON THE NET DRAW SODIUM BISULFITE CONCENTRATION

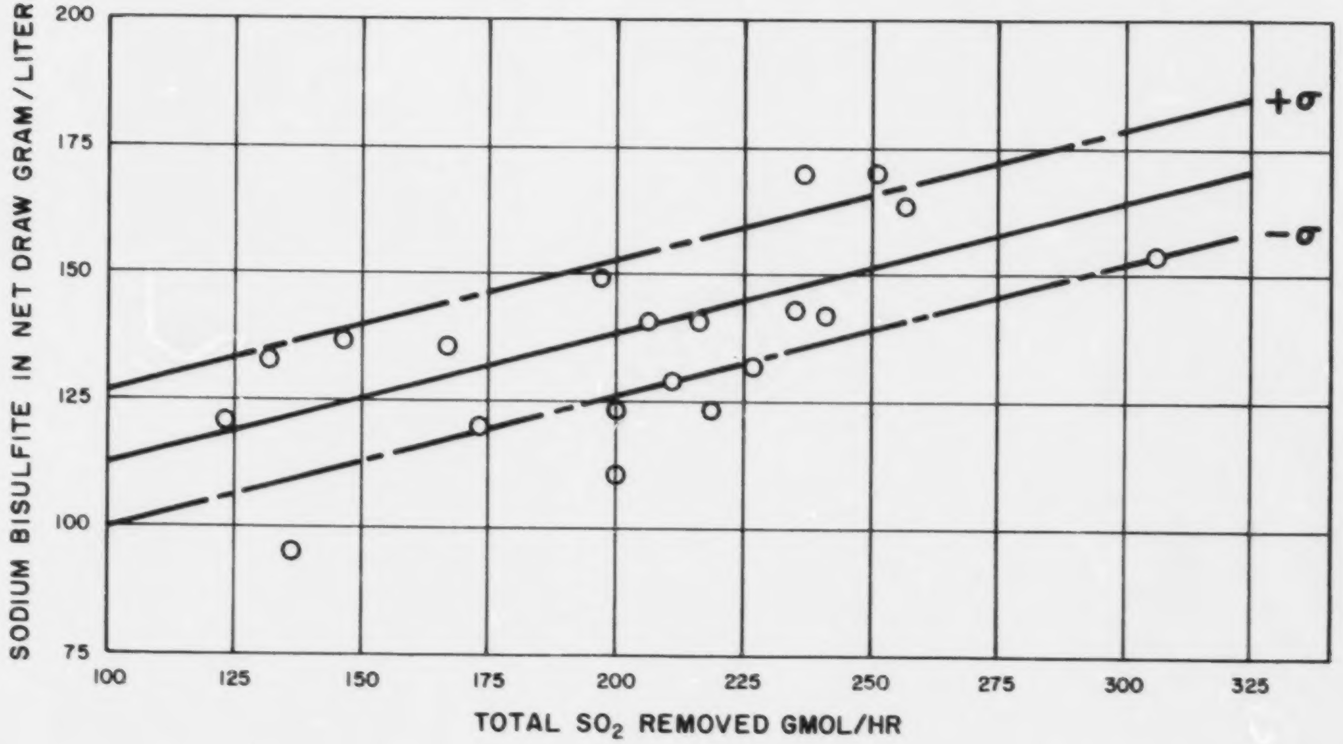


FIGURE 6.13 THE EFFECT OF TOTAL SO_2 REMOVED ON THE NET DRAW SODIUM BISULFITE CONCENTRATION

concentration, and total SO2 removal on the absorber net draw bisulfite concentration. The SO2 inlet concentration strongly influenced the ultimate bisulfite concentration in the net draw liquor. This was expected since the high SO2 partial pressures drove the absorption reactions to completion. The net draw bisulfite concentration is plotted against oxidation in Figure 6.14 and it can be seen that as the bisulfite concentration increased, oxidation decreased. Figure 8.1 (Section 8) shows the distribution of sulfate and bisulfite as a fraction of pH. The lower the pH, the more sodium bisulfite present in the system and the lower the oxidation. This result agrees with the work done by Fuller and Crist(1), and is consistent with the work of Potts, et al.(6) for unsaturated solutions. Typically, the Pilot Plant absorber net draw pH varied between 5.5 and 6.0.

The effect of alkalinity on the amount of oxidation is made clear from the basic oxidation reaction mechanism.

$$\mathrm{Na2SO3 + 1/2O2} \longrightarrow \mathrm{Na2SO4} \qquad (1)$$

$$\mathrm{NaHSO3 + NaOH} \longrightarrow \mathrm{Na2SO3 + H2O} \qquad (2)$$

$$\mathrm{NaHSO3 + 1/2O2 + NaOH} \longrightarrow \mathrm{NA2SO4 + H2O} \qquad (3)$$

The oxidation reactions (1) and (3) are influenced by the sulfurous acid equilibria of reaction (2) and oxidation can only occur to the extent that sodium sulfite exists in the system. This is consistent with the findings of the pilot plant. Sodium sulfite is the oxidized compound and minimizing the sulfite will minimize oxidation. This also confirms the Fuller and Crist conclusion that bisulfite is not oxidizable.

The fact that sodium sulfite was the oxidized compound is reconfirmed by the analyses of the absorber interstage data. Figures 6.15 and 6.16 show that when SO2 removal in the top stage increased, both in terms of absolute SO2 removal and fraction of total SO2 removal, oxidation decreased. This shift minimized the region of sodium sulfite within the absorber and therefore minimized oxidation.

Shifting the absorption profile toward the top stage is equivalent to operating with a lower absorber net draw pH. This would result from a decrease in the amount of free sodium fed to the absorber at a certain SO2 removal. The penalty in this type of operation is a lower SO2 removal efficiency.

The effect of alkalinity also explains the increased oxidation observed when splitting the caustic flow to the absorption stages. By feeding caustic directly to the bottom stage, the overall alkalinity of the tower increased (in terms of length) and there was more sulfite in the bottom stage. Consequently the amount of oxidation

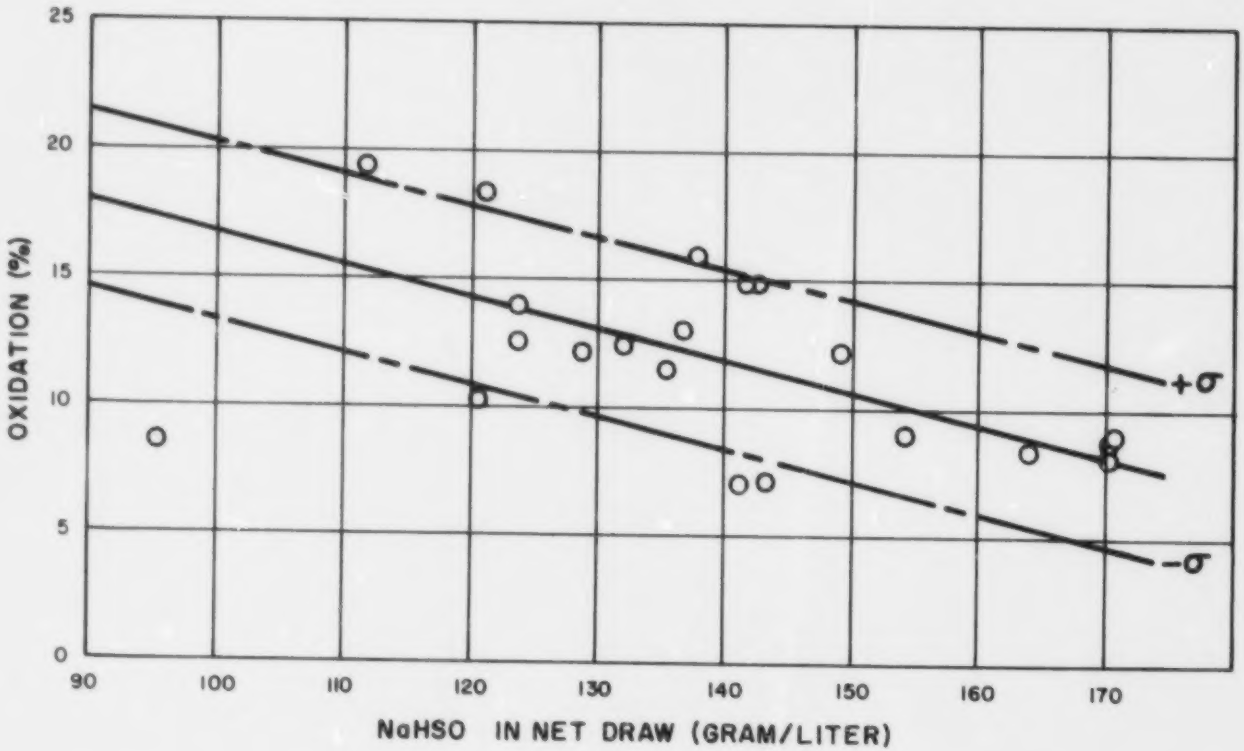


FIGURE 6.14 THE EFFECT OF ABSORBER NET DRAW SODIUM BISULFITE CONCENTRATION ON OXIDATION

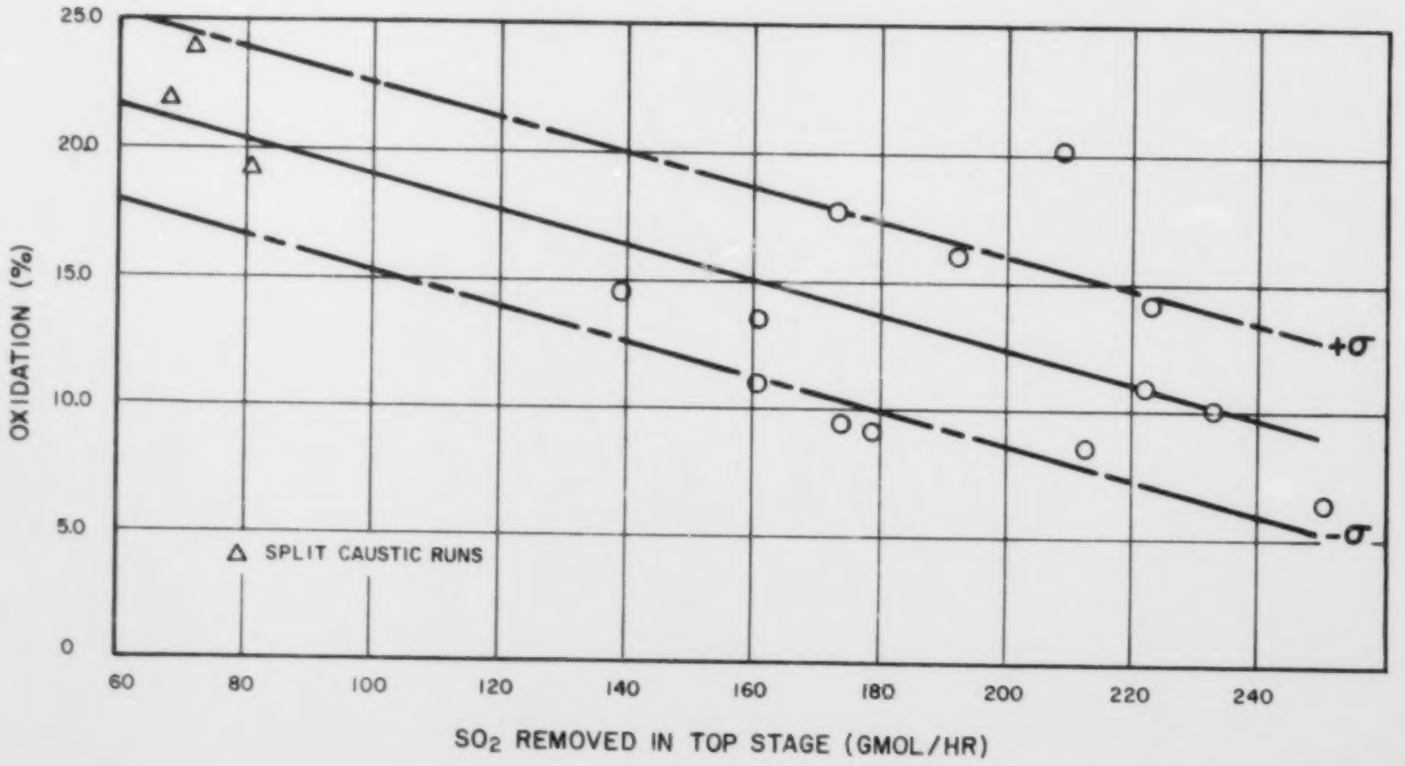


FIGURE 6.15 THE EFFECT OF SO_2 ABSORPTION PROFILE ON OXIDATION (SO_2 REMOVED IN THE TOP STAGE VS. OXIDATION)

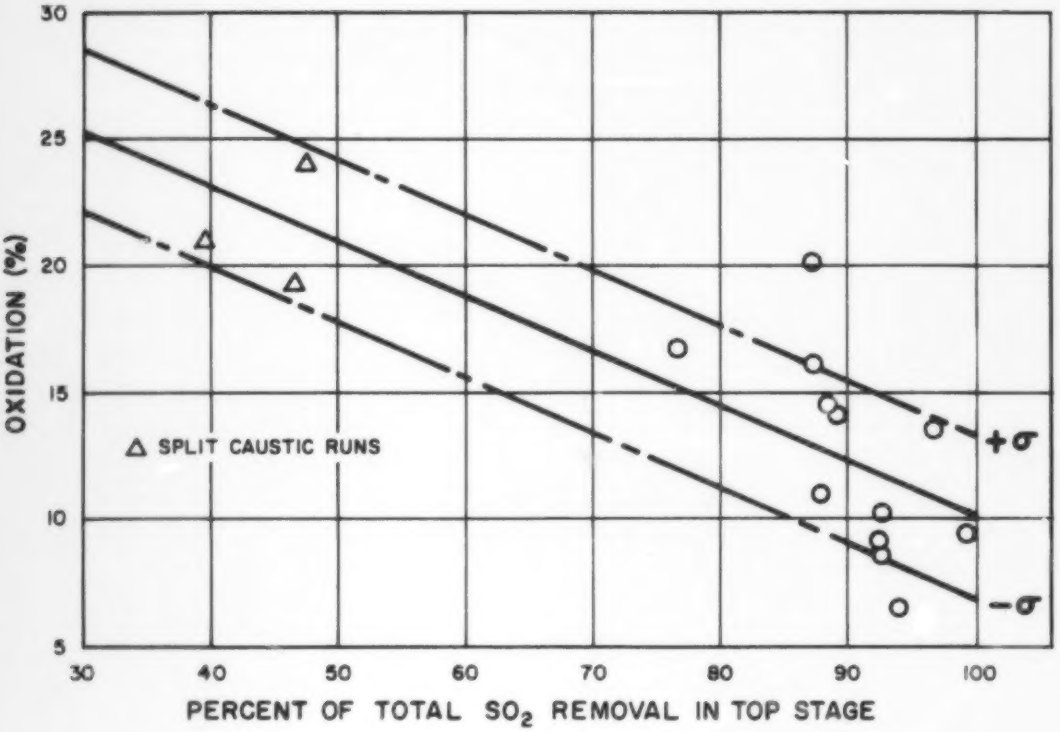


FIGURE 6.16 THE EFFECT OF SO_2 ABSORPTION PROFILE ON OXIDATION (PERCENT OF TOTAL SO_2 REMOVED IN THE TOP STAGE VS. OXIDATION)

increased. The amount of SO2 removal that occurred in the bottom stage can be related to the S/C ratio of the top stage effluent. As the S/C ratio increases, by definition, the bisulfite concentration increases (Figure 6.17) and the available sodium for SO2 removal decreases. Figure 6.18 presents the relationship between the total amount of oxidation and the S/C ratio of the top stage effluent. As the S/C ratio increased, the amount of SO2 removal in the bottom stage and the overall oxidation decreased.

The effect of the absorption profile on oxidation can be demonstrated by considering the fraction of the total oxidation that occurred in the top stage. Figure 6.19 shows that as the absolute amount of SO2 removal in the top stage increased the fraction of the total SO2 oxidized in the top stage increased. Therefore, as the absorption profile shifted toward the top stage, the amount of oxidation that occurred in the whole tower decreased and that oxidation occurred preferentially in the top stage (compare Figures 6.15 and 6.19). In other words, shifting the absorption profile toward the top stage maximized the sodium bisulfite in the top stage (Figure 6.20) and thus minimized oxidation.

In summary, oxidation was minimized by operating the absorption tower with maximum sodium bisulfite levels consistent with a desired SO2 removal.

The literature indicates that oxidation is controlled by the liquid phase mass transfer resistance for oxygen absorption. Thus, oxidation should be affected by those parameters that affect the mass transfer of oxygen, namely the gas-liquid contact time and the liquid phase viscosity, density, and turbulence.

Oxidation was plotted against the total salt concentration of the net draw, as shown in Figure 6.21. There appeared to be no effect on oxidation as the sodium sulfate concentration increased from 2.5 to 3.5 gm-mole per liter. Chertkov(4) noted an effect of salt concentration on oxidation and related it to increased solution viscosity. However Chertkov's study involved solutions considerably more dilute (10 to 15 weight percent salts versus 20 to 25 percent) and it was also an Mg system.

Residence time however had a very noticeable effect on oxidation. A hypothetical residence time was defined as the stage circulation rate in gallons per minute divided by the total free sodium feed rate to the absorber in gm-moles per hour. While the units have no significance, this "time" can be visualized as the number of times a given volume of solution contacts the oxygen-laden flue gas before it is changed over with fresh absorbing liquor. Figure 6.22 shows that as this "time" increases, oxidation increases. The ratio was multiplied by 3/2 for the split caustic runs to

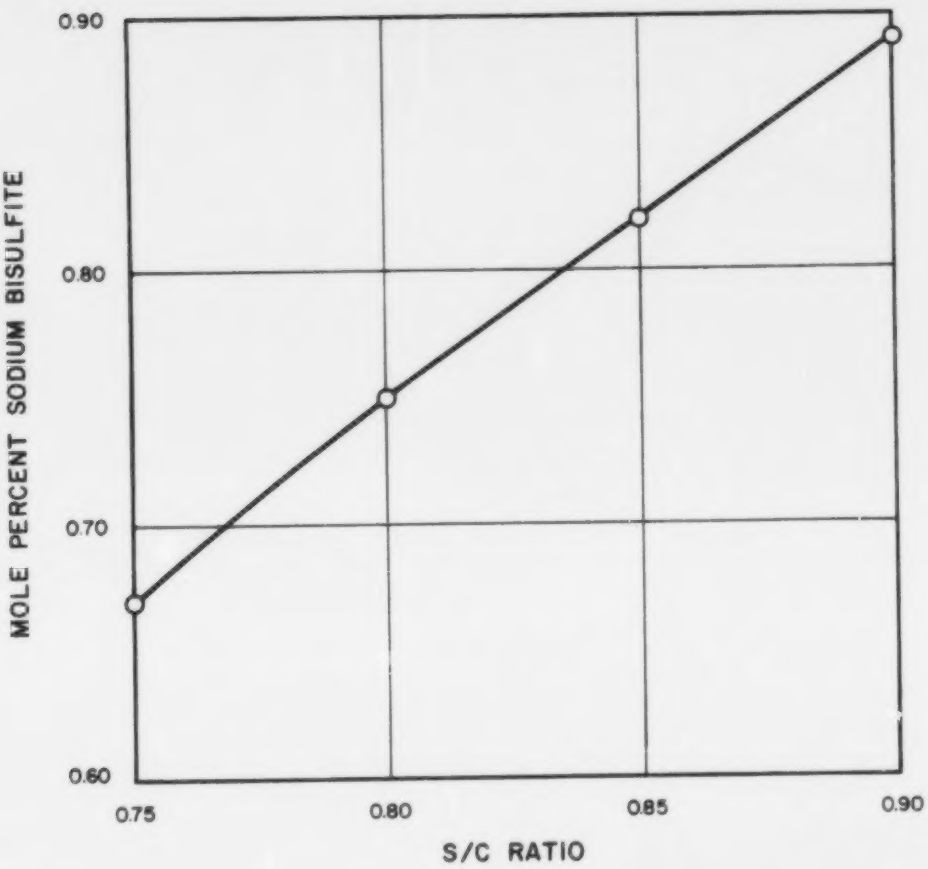


FIGURE 6.17 MOLE PERCENT SODIUM BISULFITE VS. S/C RATIO

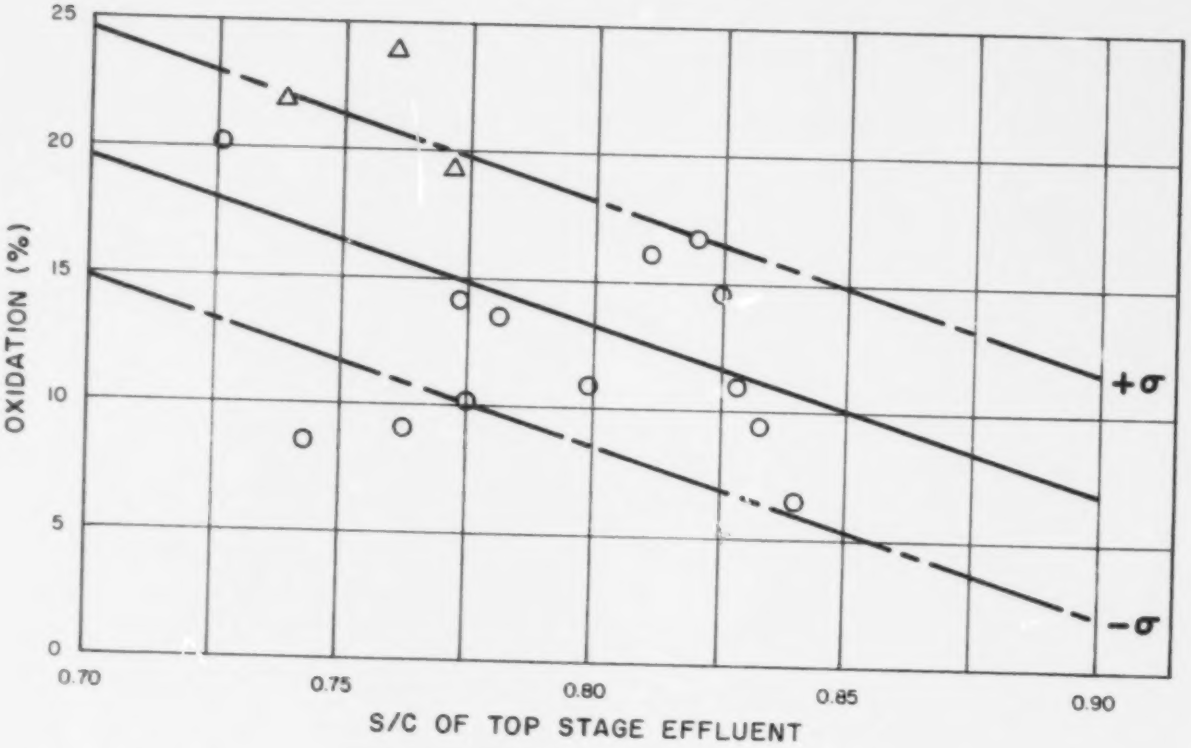


FIGURE 6.18 THE EFFECT OF SO_2 ABSORPTION PROFILE ON OXIDATION (THE S/C OF TOP STAGE EFFLUENT VS. OXIDATION)

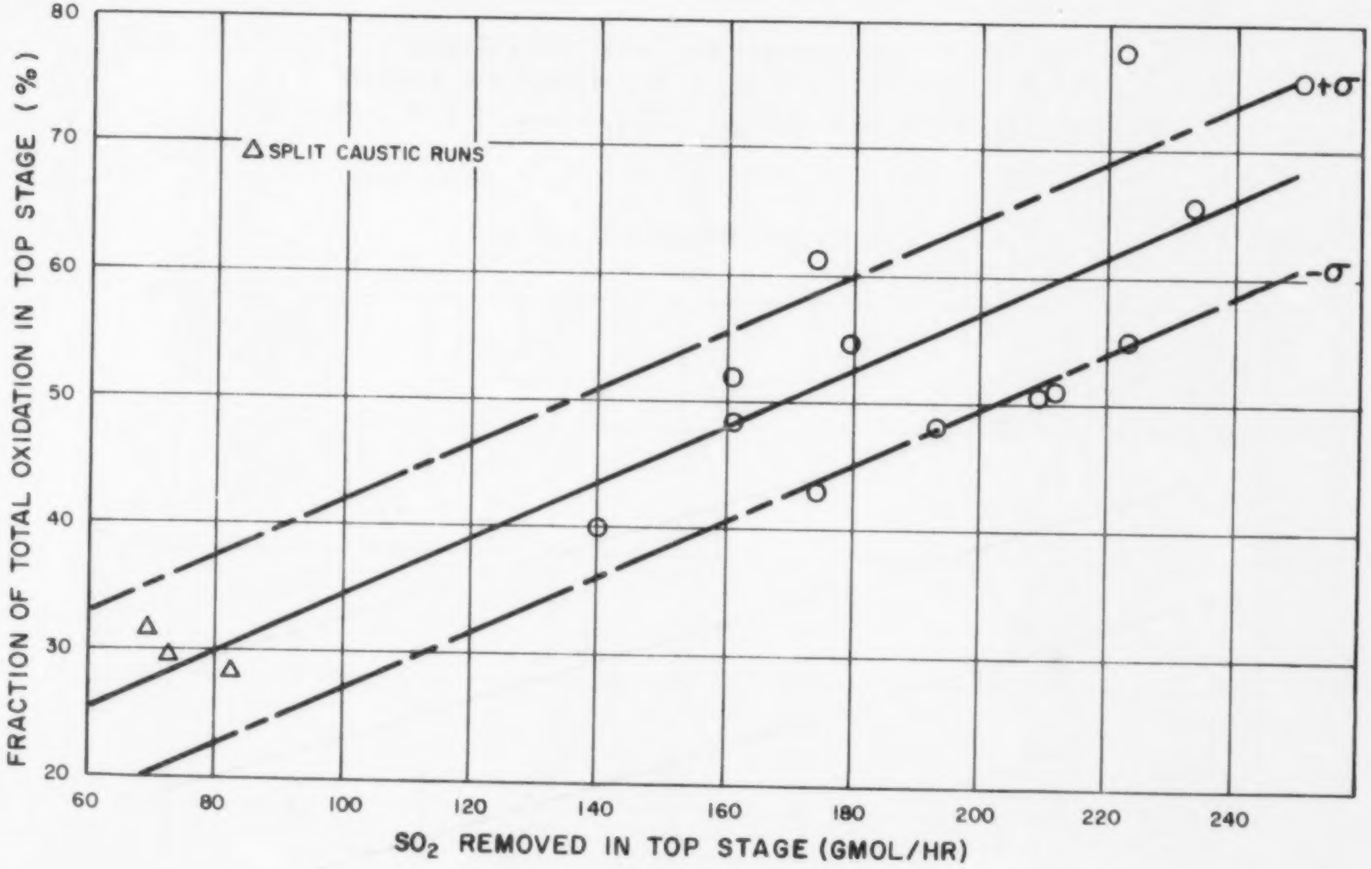


FIGURE 6.19 THE EFFECT OF SO_2 ABSORPTION PROFILE ON OXIDATION (TOTAL SO_2 REMOVED IN TOP STAGE VS. FRACTION OF TOTAL OXIDATION THAT OCCURRED IN THE TOP STAGE)

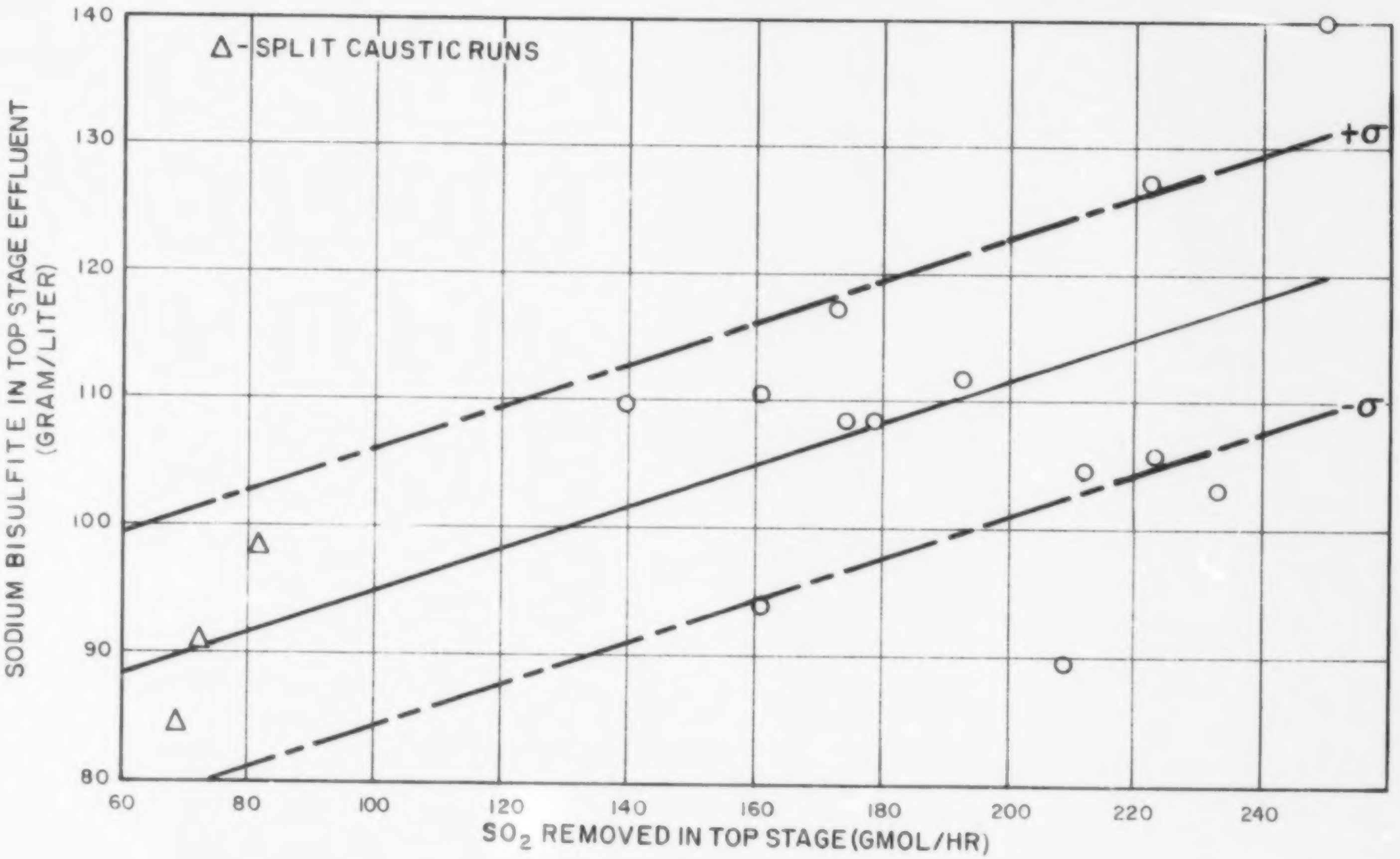


FIGURE 6.20 SO_2 REMOVED IN TOP STAGE VS. SODIUM BISULFITE CONCENTRATION IN TOP STAGE EFFLUENT

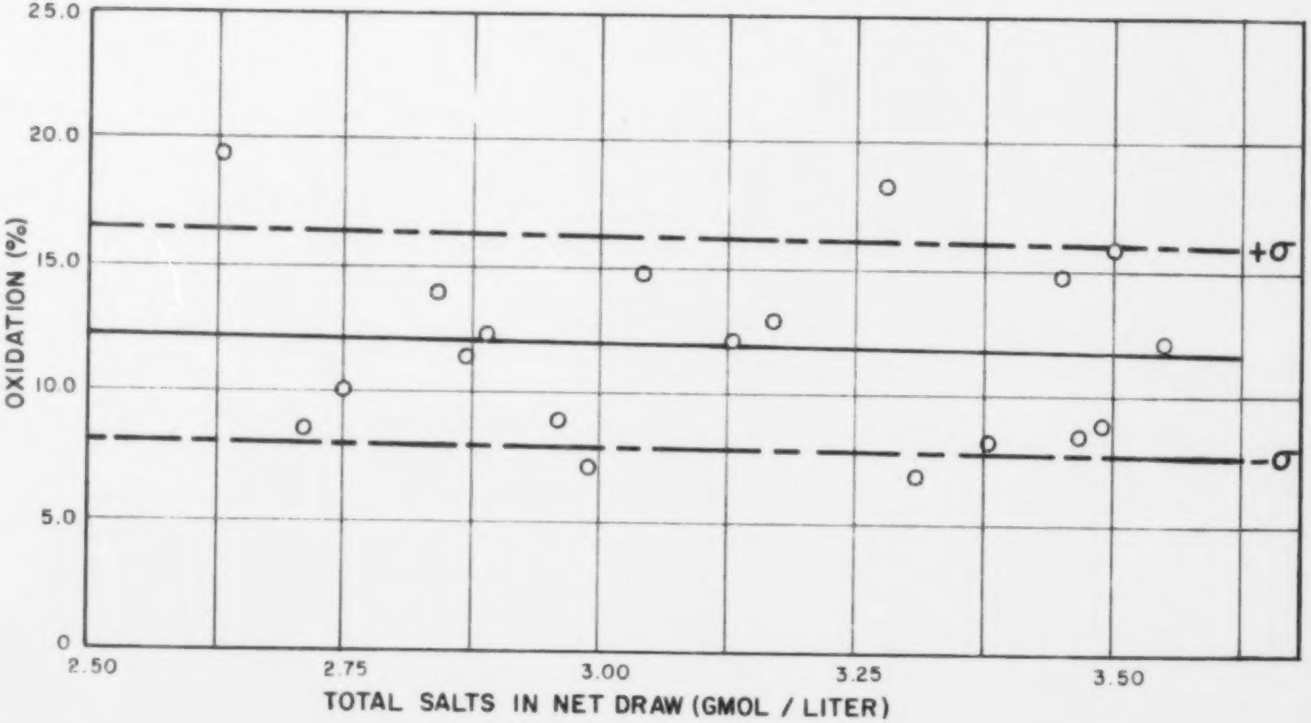


FIGURE 6.21 THE EFFECT OF TOTAL SALT CONCENTRATION IN ABSORBER NET DRAW ON OXIDATION

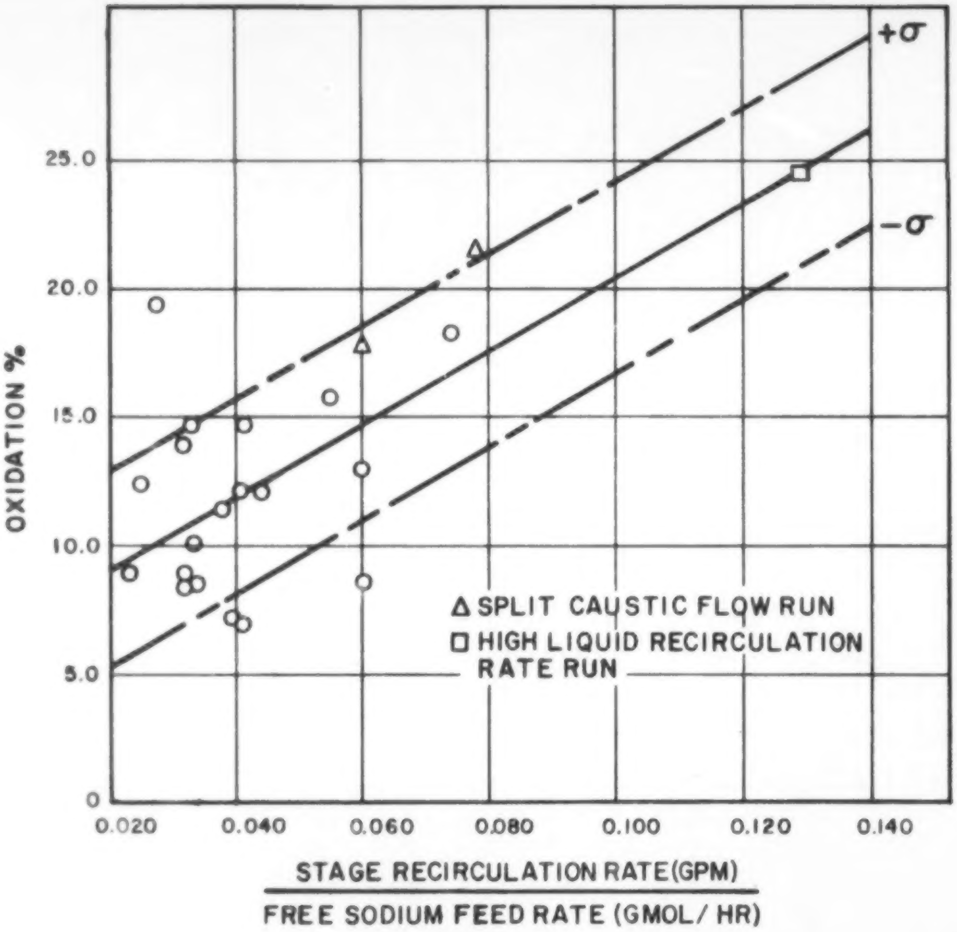


FIGURE 6.22 THE EFFECT OF GAS-LIQUID CONTACTING ON OXIDATION

reflect the increased changeover time with only half the caustic flow to the top section. Figure 6.22 also incorporates the high liquid recirculation rate run (run 27). The effect of liquid recirculation rate on oxidation could not be isolated since only one run was made at high liquid circulation rates. However, based upon the effect of contact time and the results of the high circulation rate run, oxidation should be minimized at the minimum recirculation rate required to wet the packing. An associated variable which should also affect oxidation is the volume of a particular type of packing. Although not specifically studied during the test program, gas-liquid contact beyond that required to achieve the desired SO2 removal would increase oxidation due to increased oxygen absorption by the liquor.

Figure 6.23 shows the effect of iron concentration in the caustic feed on oxidation. As the iron content increased, the level of oxidation increased. This agrees with literature results on the catalysis of sulfite oxidation by heavy metals. The iron levels in the caustic were not monitored frequently and the values reported are based upon a single measurement for an entire run. The source of the iron contamination appears to be the steel cathodes in the electrolytic cells. Cell membrane cross leaks, caused by the crystallization discussed in Section 6.4, caused corrosion in several compartments leading to the contamination of the caustic feed to the absorber. Fluctuation in these iron levels occurred as a result of cell operation, but qualitatively the effect of the iron content on oxidation proved significant. It should be noted, however, that for most runs, the iron levels in the caustic were less than 0.5 mg/l indicative of a low degree of contamination. Proper cell operation and materials of construction should allow operation at contamination levels below 0.1 mg/l.

In summation, oxidation appears to be significantly affected by the characteristics of the absorbing liquor and the extent of gas-liquid contact. Minimizing sodium sulfite within the absorber, both in terms of concentration and residence time, minimizes oxidation.

Additionally, minimizing the amount of gas-liquid contacting to only that necessary for good absorption should minimize oxidation. The effect of oxygen concentration in the flue gas as well as the type and volume of absorber packing which determine the contacting surface area were not studied as part of this program but should affect oxidation as indicated above.

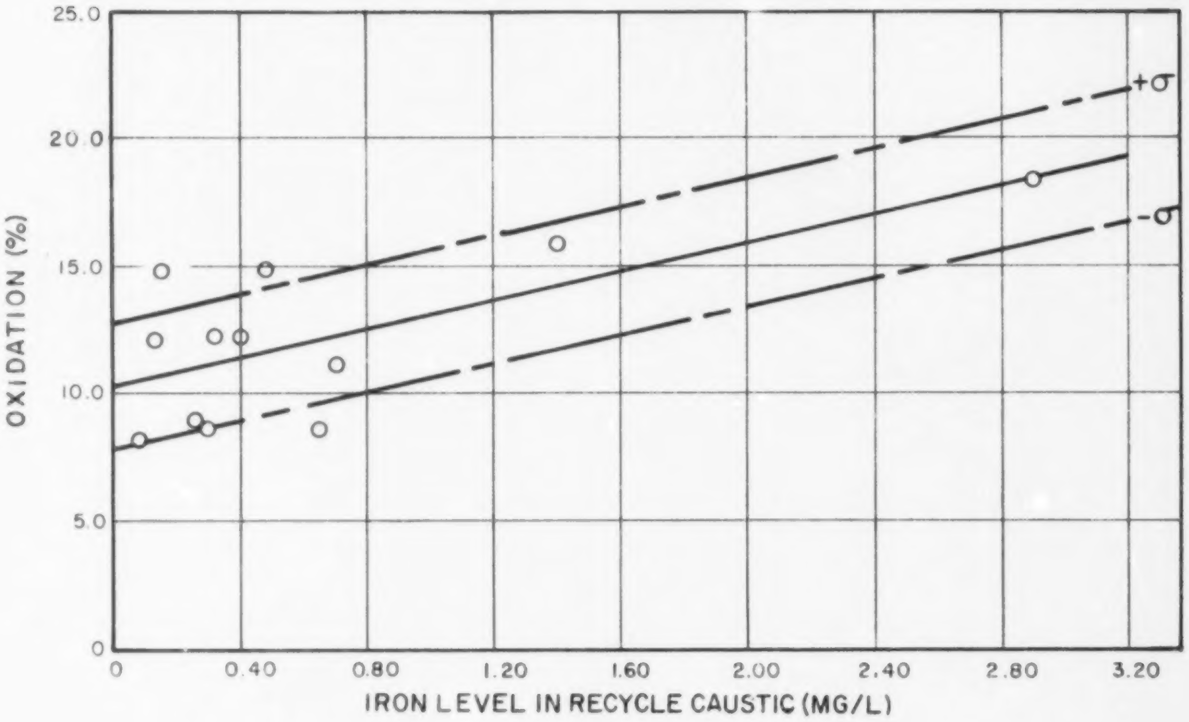


FIGURE 6.23 THE EFFECT OF HEAVY METALS CONTAMINATION ON OXIDATION

6.3 STRIPPING

The net draw liquor from the absorption section was acidified with recycle sulfuric acid releasing the SO2 in the sodium sulfite/sodium bisulfite mixture. The released SO2 is then stripped from the liquor using indirect steam. The acidification reactions are as follows:

$$Na_2SO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + SO_2 + H_2O \quad (4)$$
$$2NaHSO_3 + H_2SO_4 \longrightarrow Na_2SO_4 + 2SO_2 + 2H_2O \quad (5)$$

Any SO2 oxidized in the absorber was fixed as sodium sulfate and could not be released. The total acid consumption will be less than the caustic consumption by that amount. The resultant increase in sulfate ions within the system makes a "B" cell acid purge necessary to maintain the overall acid-base balance.

The required stripping steam rate and effectiveness of acid addition were studied during the test program. A more detailed study was not possible because of a lack of instrumentation. There were no liquid flowmeters on either the feed or effluent flows and the overhead gas flowmeter was plagued with problems throughout the test program.

6.3.1 Stripping Steam Rate

Figure 6.24 presents the stripping steam rate (as a function of SO2 removed from the flue gas) versus the residual SO2 levels in the net stripper bottoms.

The minimum steam required for the reboiler including heat losses and feed preheat requirement was about 6 lb steam per pound of SO2 removed. Estimates of the preheat required to raise the feed from 110 F to 235 F were made. Of the measured steam flow of 6 lb per pound of SO2, 4.25 pounds can be accounted for as process preheat. The remainder is process stripping steam and heat losses. If the steam equivalent of this duty is subtracted from the total steam fed to the reboiler, the resultant stripping steam required is 1.0 to 2.0 lb per pound of SO2 removed including heat losses. The final design steam rate will depend upon the heat exchange method chosen. Based upon absorption data for the SO2 -H2O system, a minimum of about 0.5 -1.0 lb of steam per pound of SO2 removed is required for stripping. This is exclusive of heat losses and the solubility depression of sodium sulfate in the liquor.

Theoretical transfer unit heights could not be calculated due to the lack of reliable flow rate data.

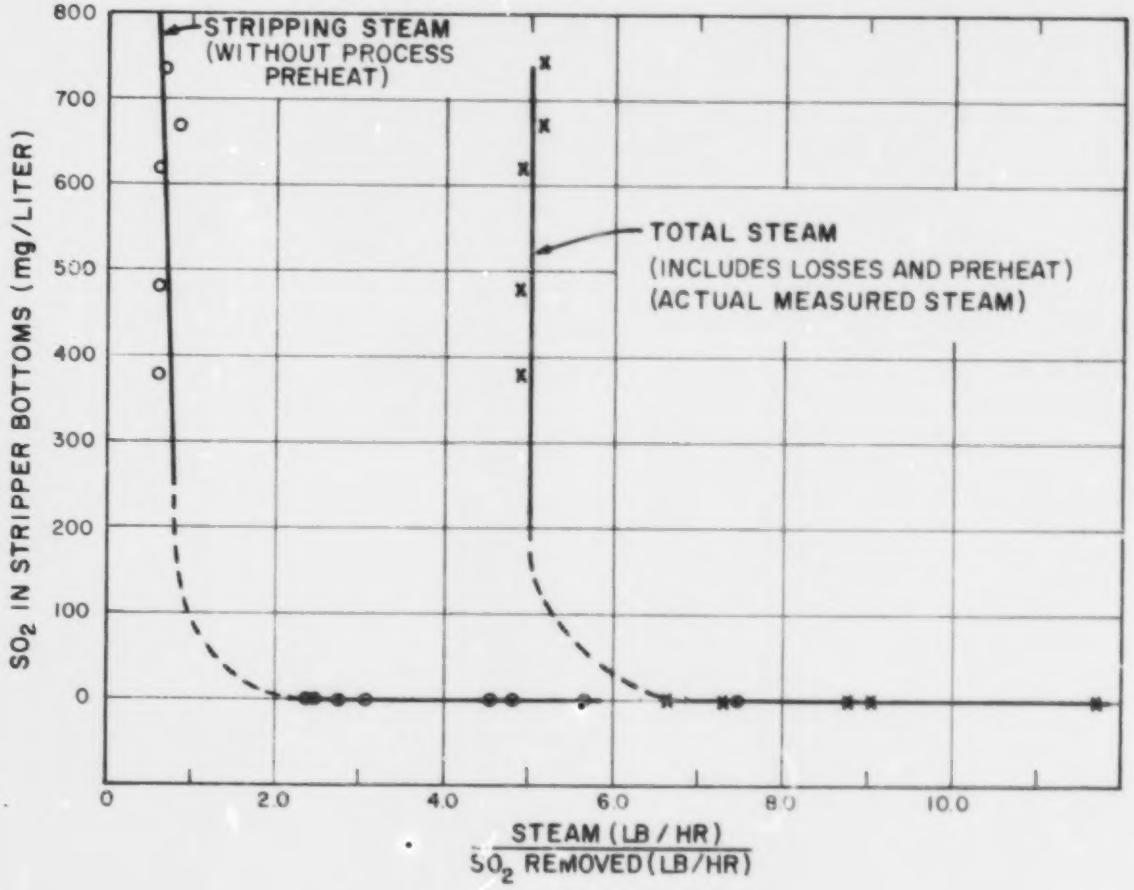


FIGURE 6.24 LIMITING STRIPPING STEAM AS A FUNCTION OF SO_2 CONCENTRATION IN STRIPPER BOTTOMS

It should be noted that the stripping steam tests were performed after the bottom eight-foot packed section had dropped into the reboiler drum. The support tray for the bottom stage may have failed as a result of the rupture disc relieving several times previously.

6.3.2 Acid Addition

The addition of the stoichiometric amount of acid to the net draw liquor was an important part of the overall process economics. Since cell feed liquor pH must be about 8.5 for iron and aluminum removal, any excess acid addition to stripper feed must be neutralized with recycle caustic. This results in an increase in the number of electrolytic cells required for a given SO2 removal.

Conversely, if less than the required amount of acid is added, unreleased SO2 (above 200 ppm) will remain in the stripper bottoms. The oxidation of ferrous iron to ferric iron takes place in the feed liquor treatment section. Any large excess SO2 must also be oxidized to ensure the oxidation of divalent to trivalent iron. This would result in increased peroxide costs as well as additional "B" cells for removal of the additional sulfate formed.

Based on operating conditions from Table 6.2, 400 milligrams per liter of SO2 in the stripper bottoms is the equivalent of 1.0 percent oxidation. Additionally, an excess acid level of 0.05 g-moles per liter in the stripper bottoms is equivalent to 16 percent excess acid flow in the absorber net draw.

The acid addition to the net draw stream was controlled by the pH of the stripper bottoms. The typical operating pH range was from 2.5 to 3.0.

Figure 6.25 presents the residual SO2 levels in the stripper bottoms and the excess acid in the stripper bottoms (expressed in gmoles sulfuric acid per liter of bottoms effluent) as a function of pH. This curve is based on samples taken over the entire test program and in all cases the stripping steam was well above the required minimum.

Since caustic is needed for neutralization of excess sulfate ions from SO2 oxidation as well as the excess acid, one can calculate the optimum pH for stripper bottoms operation as a function of recycle caustic required. A base case with operating conditions in accordance with Table 6.2 was assumed. For several pH levels in the stripping bottoms, the recycle caustic (as a percentage of caustic feed to the absorber) was calculated from excess acid and residual SO2

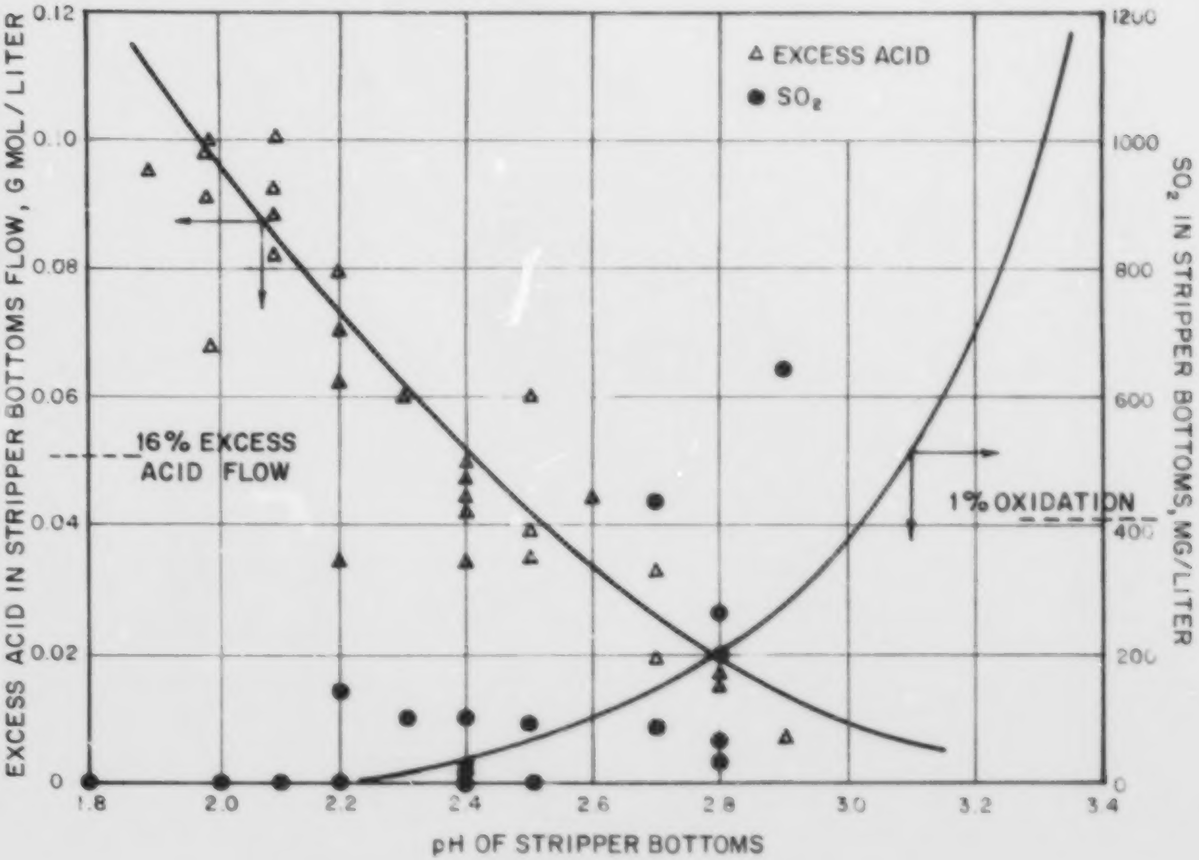


FIGURE 6.25 EXCESS ACID, RESIDUAL SO_2 IN STRIPPER BOTTOMS AS A FUNCTION OF pH

values using Figure 6.26. The optimum pH was found to be 3.2 with a minimum caustic recycle of 3.2 percent.

This does not however represent the economic minimum since peroxide costs and differential power costs ("B" cells for oxidation versus "A" cells for caustic) were not included. Incorporation of these cost figures would shift the minimum to a lower pH. Since Figure 6.25 was based on actual pilot plant data, the minimum recycle calculated is peculiar to the pilot plant operation. In future installations, additional stripping trays should be included. This would lower the caustic recycle required.

The titration curve for a sample of feed liquor (20 percent wt sodium sulfate) was determined and compared to one for water (Figure 6.27). The buffering effect of the salt solution is significant and allows pH control in the range of interest without the complex instrumentation and incremental acid or caustic addition that pure water requires.

TABLE 6.2
BASE CASE OPERATING CONDITIONS
FOR STRIPPING STUDY

Gas Rate	8000 lb/hr
SO2 Inlet	2000 ppm
SO2 Removal	90%
S/C in Net Draw	0.90
Caustic Normality	2.0
Acid Normality	1.0
Oxidation in Absorber	10%

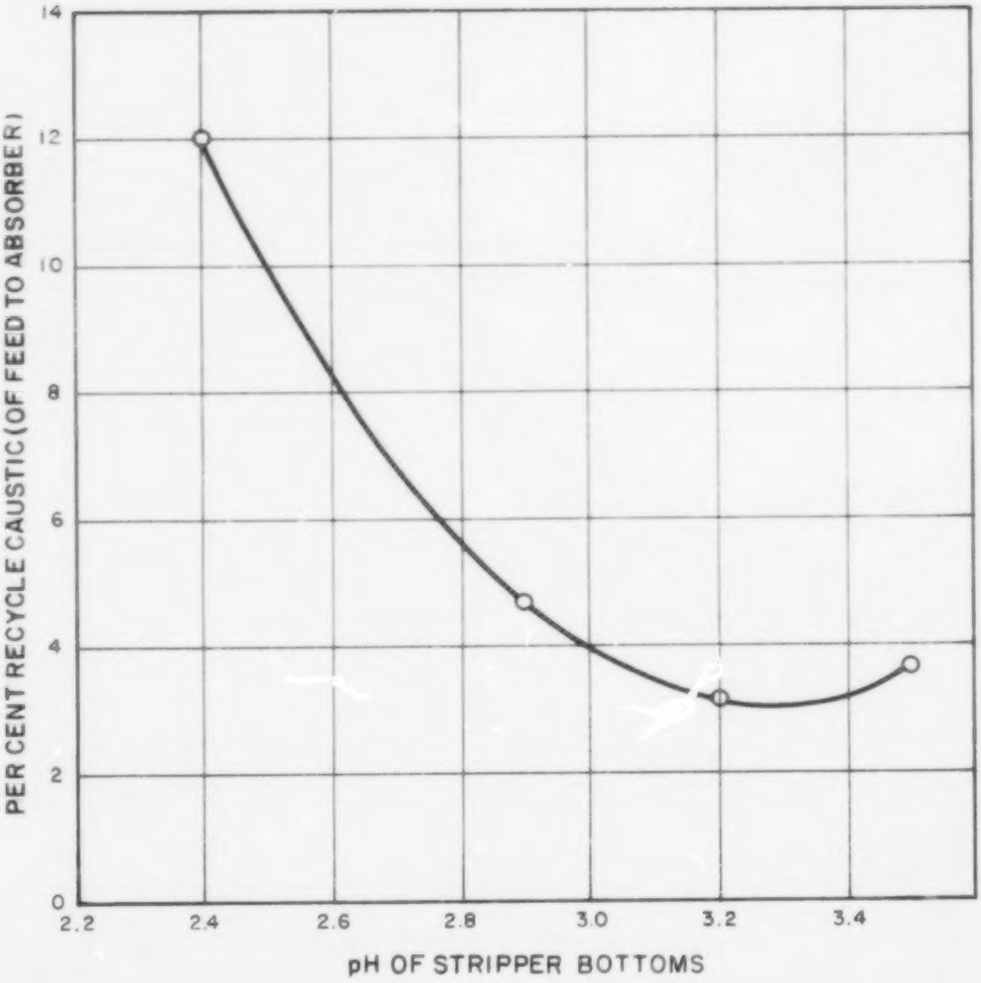


FIGURE 6.26 OPTIMUM pH FOR STRIPPER BOTTOM OPERATION (EXCLUDING COST FACTORS)

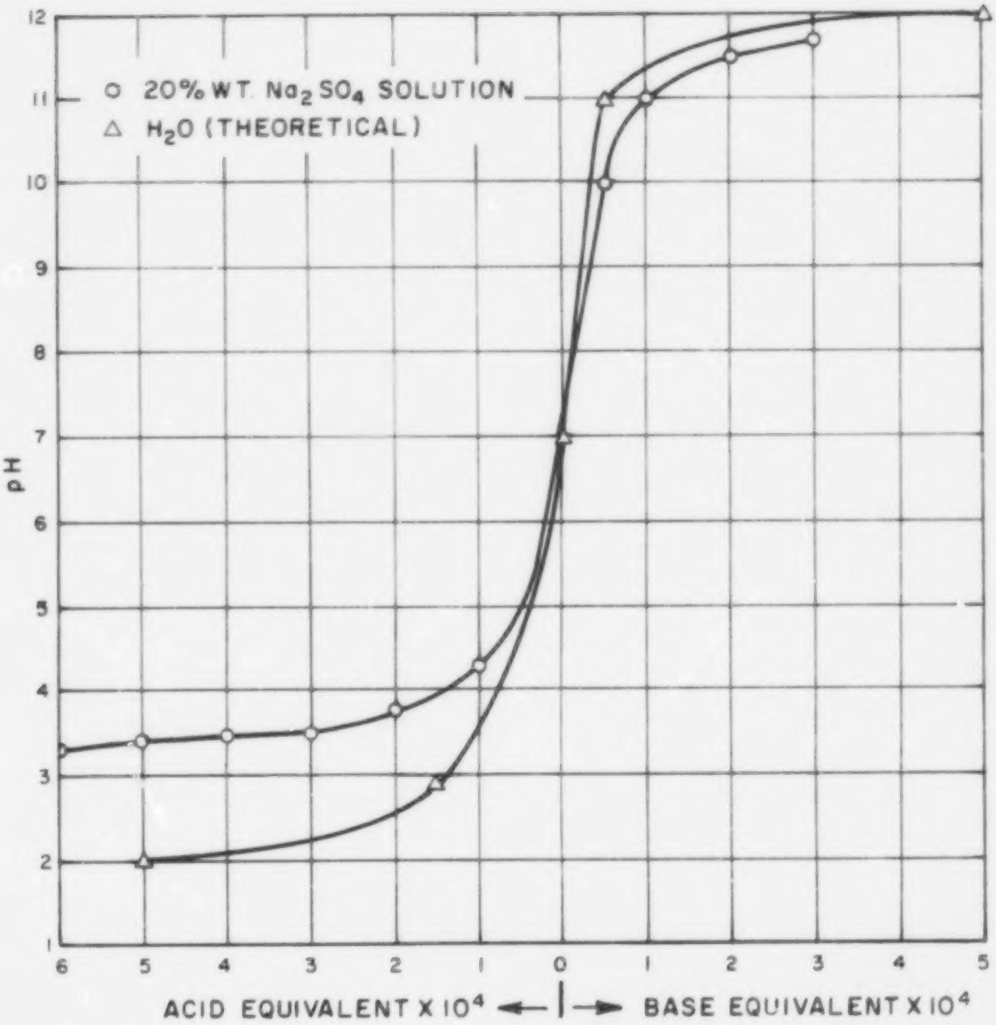


FIGURE 6.27 TITRATION CURVE–SODIUM SULFATE SOLUTION VS. WATER
SAMPLE SIZE: 50 ml

6.4 ELECTROLYTIC REGENERATION

6.4.1 General Description of the Cell System

The primary function of the electrochemical cells is to electrolyze the sodium sulfate solution from the stripper bottoms to produce caustic soda (admixed with sodium sulfate) for recycle to the absorber, and sulfuric acid (also admixed with sodium sulfate) for recycle to the stripper. In addition, the cells produce a stream of dilute, essentially sodium-free sulfuric acid to purge from the overall system the sulfuric acid which forms in the absorber from sulfur trioxide in the stack gas and by oxidation of some absorbed SO2.

Two types of cells are used in the process; they are shown schematically in Figure 6.28 (Note: both types of cells employ a second diaphragm adjacent to the cathode to enhance the current efficiency). The Type "A" electrolytic cell is the basic cell and contains three major compartments. The Type "B" cell is merely a variation of the "A" cell and is formed by adding an anion membrane adjacent to the anode. This membrane blocks the passage of sodium ions and therefore allows a part of the acid to be produced free of sodium.

The hydraulic system associated with the cells provides the following:

a) Monitors, controls, distributes, and collects the various streams that flow to and from the cells

b) Provides for efficient gas/liquid separations

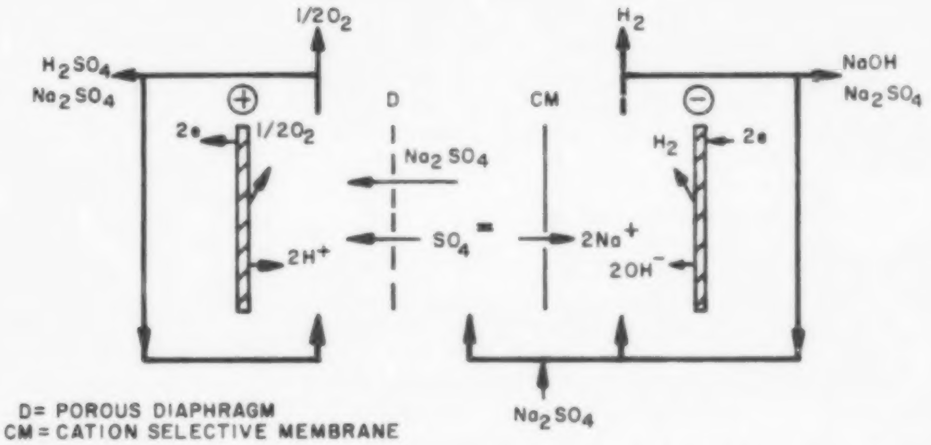
c) Provides cell cooling

Rectification equipment converts a-c input to d-c energy which is then distributed to each of the electrochemical cells in the pilot plant. A control panel provides for power distribution to the pump and blower motors as well as monitoring and controlling the overall cell system.

6.4.2 Cell System Design Point

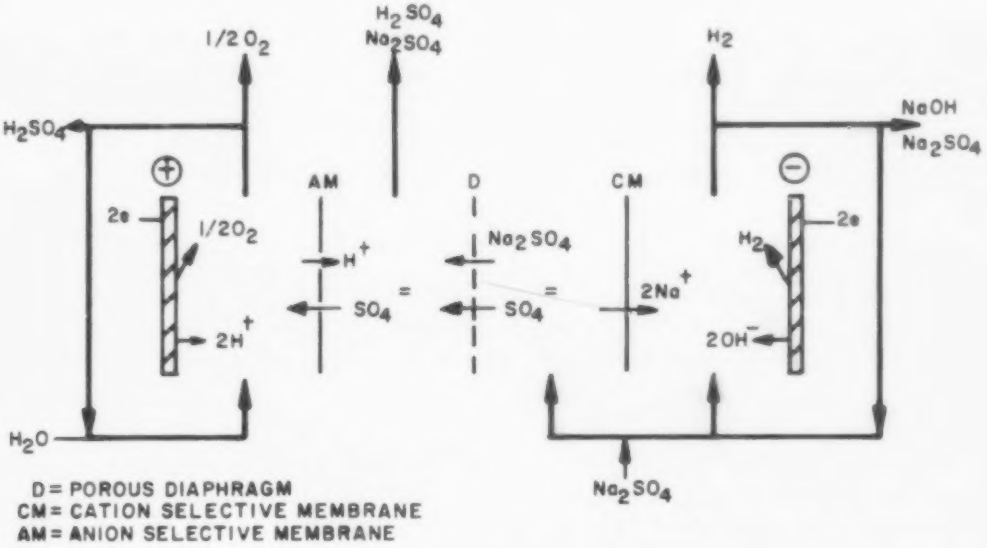
The cell system for the WEPCO pilot plant was sized to produce 0.79 lb/mole/hr of NaOH and 0.063 lb/mole/hr of sodium-free H2SO4. Fifty-six "A" and 32 "B" cells, operating at current densities of 142 amperes per square foot of effective electrode area (ASF) and 127 ASF, respectively, are required to fulfill the production rates. Each cell has an effective electrode area of 0.945 square feet. Other selected design values for the pilot plant are summarized in Table 6.3.

Design point material balances for the 56 "A" cells and 32 "B" cells are given in Figures 6.29 and 6.30, respectively.


1/2O2
H2
H2SO4
Na2SO4
NaOH
Na2SO4
+
D
CM
−
2e
1/2O2
Na2SO4
H2
2e
2H+
SO4=
2Na+
2OH−
Na2SO4

D= POROUS DIAPHRAGM
CM = CATION SELECTIVE MEMBRANE

FIGURE 6.28A SCHEMATIC DIAGRAM OF "A" ELECTROLYTIC CELL


1/2 O2
H2SO4
Na2SO4
H2
H2SO4
NaOH
Na2SO4
+
AM
D
CM
−
2e
1/2O2
H+
Na2SO4
H2
2e
SO4=
SO4=
2Na+
2H+
2OH−
H2O
Na2SO4

D = POROUS DIAPHRAGM
CM = CATION SELECTIVE MEMBRANE
AM = ANION SELECTIVE MEMBRANE

FIGURE 6.23B SCHEMATIC DIAGRAM OF "B" ELECTROLYTIC CELL

Table 6.3

SELECTED DESIGN VALUES OF WEPCO PILOT PLANT

	"A" Cells	"B" Cells	Total
No. of Cells	56	32	88
Active Electrode Area (0.945 sq.ft.per cell),sq.ft.	52.9	30.2	83
No. of Stacks	2	1	3
Cells per Stack	32 & 24	32	-
Cells per Electric Module	8	8	-
Maximum Current Density, ASF	180	180	-
Design Current Density, ASF	142	127	-
Stack Current, amps	1074	960	-
Cell Voltage, volts	6.48	6.63	-
Total Power, KWDC	48.7	25.5	74.2
DC Energy per lb NaOH,[(a)] kw hr/lb NaOH	2.32	2.37	2.34
Production Rates, lb-mole/hr			
NaOH in mixed caustic	0.525	0.269	0.794
H_2SO_4 in mixed acid	0.263	0.071	0.334
H_2SO_4 as pure dilute acid	0	0.063	0.063
Make-up Water,[(b)] lb-mole/hr	0	3.56	3.56
GPM	0	0.128	0.128
Cooling Requirements[(c)]			
Anolyte, Btu/hr	47,800	23,300	71,100
Catholyte, Btu/hr	31,900	15,500	47,400
Cooling Water (d) GPM	5.3	2.6	7.9

(a) Phase I Performance Objectives (3$\underline{N}$ Na_2SO_4 feed solution, 140°F, 85% NaOH current efficiency) adjusted downward for the above Design Current Densities.

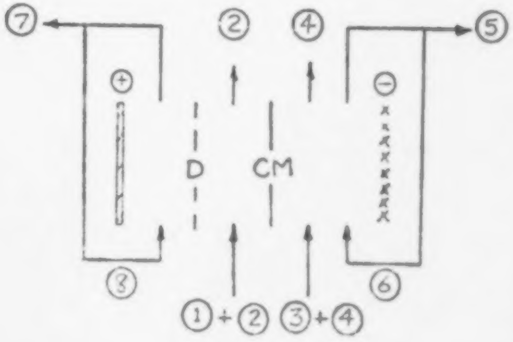
(b) Consists of water fed to the anolyte of "B" cells only.

(c) Based on above cell voltages less 2 volts reversible voltage. Sodium sulfate solution assumed fed at 100° F and make-up water at 80° F. Latent heat of vaporization of water at electrodes taken into account but losses to environment neglected. Total cooling split 60-40, anolyte-catholyte.

(d) Based on 30° F temperature rise of cooling water.

FIGURE 6.29 Design Point Material Balance for 56 Type "A" SULFOMAT Cells of WEPCO SO_2 Removal Pilot Plant.

	1		2		3		4		5		6		7		8		9		10	
	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
NaOH									21.0	.525	232	5.80								
Na_2SO_4	171.3	1.206	5.35	.0377	69.0	.486	5.35	.0377	69.0	.486	761	5.36	133.9	.943	2244	15.80				
H_2SO_4													25.8	.263	431	4.40				
H_2O Liquid	567	31.5	17.73	.985	228	12.67	17.73	.985	263	14.62	2903	161.3	515	28.6	8622	479				
H_2O Vapor									1.197	.0637			.574	.0319						
H_2									.618	.309										
O_2													4.94	.1545						
Totals	738		23.1		297		23.1		355		3896		680		11297					
GPM	1.203		.0377		.484		.0377		.526(liq)		5.81		1.051(liq)		17.59					
Sp. Gr.	1.227		1.227		1.227		1.227		1.342(")		1.342		1.285(")		1.285					
Temp, °F	100		100 – 140 in out		100		100 - 140 in out		140		130-140 in out		140		135-140 in out					
Press, psia	–		–		–		–		17.0		–		17.0		–					
CFM, CPT	–		–		–		–		2.35(gas)		–		1.177(gas)		–					



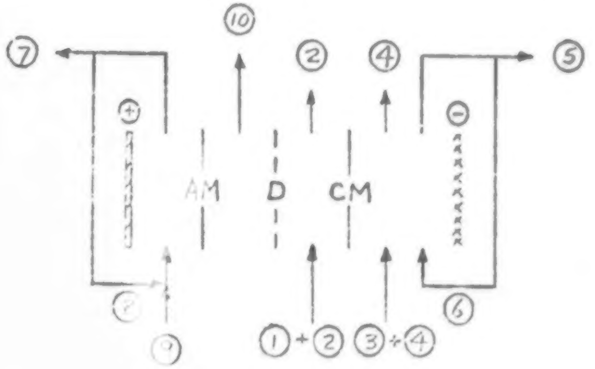
Basis:

56 "A" Cells, 0.945 sq. ft. ea., 52.9 sq. ft.

Feed Normality = 4 N Na_2SO_4
Current Density = 192 ASF
NaOH Current Efficiency = 85 %
Purged H_2SO_4 Current Efficiency = N/A %
Operating Temperature = 140 °F
Catholyte Caustic Normality = 2 N
Anolyte Acid Normality = 1 N
Mid-Anolyte Acid Normality = N/A N

FIGURE 6.30 Design Point Material Balance for 32 Type "3" SULFOMAT™ Cells of WEPCO SO_2 Removal Pilot Plant

	1		2		3		4		5		6		7		8		9		10	
	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
NaOH									10.76	.269	118.8	2.97								
Na_2SO_4	87.6	.617	2.74	.0193	35.4	.249	2.74	.0193	35.4	.249	390	2.75							68.6	.483
H_2SO_4													6.20	.0633	441	4.50			6.97	.0711
H_2O Liquid	290	16.12	9.07	.504	116.8	6.49	9.07	.504	134.6	7.48	1487	82.6	61.0	3.39	4338	241	64.1	3.56	267	14.82
H_2O Vapor									.587	.0326			.293	.0163						
H_2									.317	.1553										
O_2													2.53	.0791						
Totals	378		11.8		152.2		11.8		181.7		1996		70.0		4779		64.1		343	
GPM	0.616		.0192		.248		.0192		.269 (liq)		2.98		.127 (liq)		9.01		.128		.540	
Sp. Gr.	1.227		1.227		1.227		1.227		1.342 (")		1.342		1.061 (")		1.061		1.00		1.270	
Temp, °F	100		100 - 140 in out		100		100 - 140 in out		140		131 - 140 in out		140		135 - 140 in out		80		140	
Press, psia	—		—		—		—		17.0		—		17.0		—		—		—	
CFM, OPT	—		—		—		—		1.204 (gas)		—		.602 (gas)		—		—		—	



Basis:

32 "B" Cells, 0.945 sq. ft. ea., 30.2 sq. ft.

Feed Normality = 4 N Na_2SO_4

Current Density = 127 ASF

NaOH Current Efficiency = 85 %

Purged H_2SO_4 Current Efficiency = 40 %

Operating Temperature = 140 °F

Catholyte Caustic Normality = 2 N

Anolyte Acid Normality = 2 N

Mid-Anolyte Acid Normality = 0.53 N

The change in cell voltage with current density, consistent with contract performance objectives, is given in Figure 6.31.

6.4.3 Cell System Operations

It is convenient in discussing the electrolytic cell system to divide the pilot plant operating time into three periods: initial cell system and process debugging period (three months), cell system evaluation period (six months), and advanced component evaluation period (three months). Each period ended with disassembling of the cells for inspection and rebuilding the cells with new membranes and diaphragms for the next period.

6.4.4 Initial Cell System and Process Debugging Period

In this period, the fully integrated SO2 removal pilot plant was operated for the first time. Process and system deficiencies and refinements were identified and corrected, and personnel became familiar with the operation of the plant.

In the electrolytic cell area, the principal problem encountered was the quality of the cell feed liquor. It was intended that dissolved iron would be removed by a manganese zeolite (MnZe) conditioner which oxidizes the ferrous ion to ferric ion and also filters out the precipitate ferric hydroxide under alkaline conditions.

The initial problems with the MnZe conditioner resulted from pH excursions in the process steam. At low pH's, iron passes through the unit and at high pH's, aluminum was leached out of the bed. Both metals in hydroxide form precipitated out mainly on the cathode diaphragms of the cells causing increasing pressures within the cells. A new automatic pH control point was therefore installed between the heat exchanger, (T-103), which is downstream of the stripper, and the sulfate surge tank, (M-101). Also, the MnZe conditioner was relocated to the electrolytic cell section of the pilot plant to permit operation at the required pH level of 8 to 9.

Subsequently, temperature excursions of the feed liquor stream occurred under the "isolate" mode of operation of the cell system and these led to degradation of the bed in the MnZe unit. Also, bed regeneration was sometimes incomplete and iron breakthrough occurred. Each upset resulted in additional deposits in the cells, affecting the internal pressure distribution. Removal of deposits was accomplished to some extent by acid-washing the catholyte diaphragms in situ, but with some detrimental effects to the cation membranes then in use.

A heat exchanger was installed to eliminate the temperature excursions under the "isolate" mode of operation. The bed

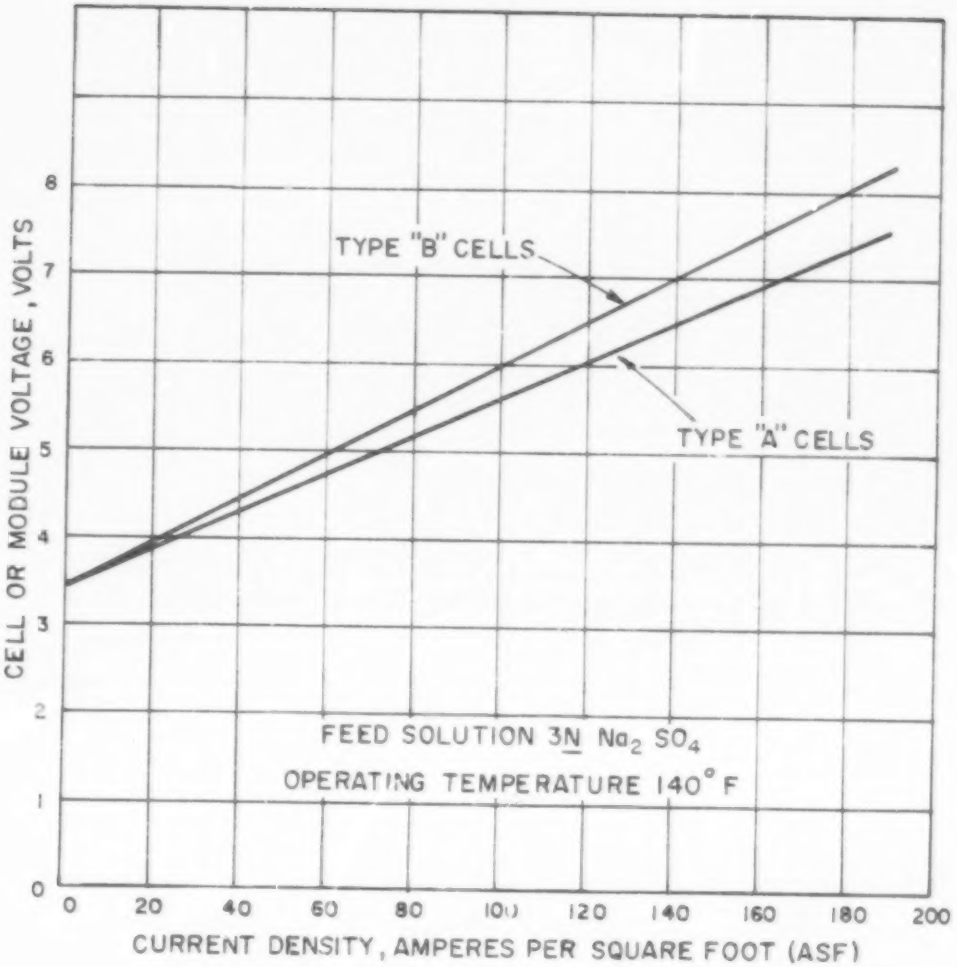


FIGURE 6.31 DESIGN CELL VOLTAGE-CURRENT DENSITY RELATIONSHIPS FOR TYPES "A" AND "B" SULFOMAT™ CELLS

of the MnZe unit was replaced and regeneration water for the unit was changed from city water to steam condensate. Deionizers were installed to treat the latter at the pilot plant due to contamination from new pipes which brought the condensate to the pilot plant area.

Because diaphragm-grade caustic, rather than rayon-grade caustic, was used inadvertently to charge the pilot plant initially, excessive chloride levels were present in all process streams. Consequently, at the end of the debugging period, process liquors were drained and new solutions were prepared using rayon-grade caustic.

Also, because of the numerous upsets that had occurred which led to deposits in the cells leading to the resulting need for in-situ acid washes and the above-mentioned excessive chloride levels throughout the period, the cells were rebuilt at the end of the period with new membranes and diaphragms. Anodes and cathodes were reused.

During the initial debugging period, the "A" cells were operated 443.5 hours and the "B" cells were operated 354 hours.

6.4.5 Cell System Evaluation Period

The bulk of the test program for the integrated pilot plant was conducted during this period. Cell operating times were 2093.5 hrs and 2089 hrs for the "A" and "B" cells, respectively. There were five continuous runs of ten days or more during this period. The longest was 13 days.

Cell operating levels varied from 70 percent to 100 percent of design levels, depending on the caustic feed rate to the absorber and the relative liquid levels in the caustic, mixed acid, and sulfate surge tanks (M-105, M-104, and M-101, respectively).

6.4.5.1 Current Efficiency Results - Current efficiency results for this period and for the final "Advanced Components Evaluation Period" are summarized in Table 6.4.

The overall performance of all the cells in the pilot plant, both "A"s and "B"s, is given by the current efficiency of the "Combined Catholytes." This measurement compares the actual amount of NaOH produced by all the cells to the theoretical amount that could be produced according to Faraday's law for the current applied to the cells. Table 6.4 shows that, for the first three-and-a-half months of the period (through C.E. No. 21), the current efficiency of the combined catholytes was consistently from 86 percent to 93 percent, and averaged 90 percent. This compares favorably with a design value of 85 percent (see Figures 6.29 and 6.30).

Table 6.4

SUMMARY OF WEPCO PILOT PLANT CURRENT EFFICIENCY MEASUREMENTS

C.F.No.	Date	H_2SO_4 Feed Conc.	A-Cells Stack Current amps	A-Cells Current Density A/F	B-Cells Stack Current amps	B-Cells Current Density A/F	Combined Catholytes Norm NaOH	Combined Catholytes C. E.	A-Cells A-Anolyte Norm. H_2SO_4	A-Cells A-Anolyte C.E.	B-Cells B-Mid Anolyte Norm. H_2SO_4	B-Cells B-Mid Anolyte C.E.	B-Cells B-Anolyte Norm.	B-Cells B-Anolyte C.E.	B-Cells B-Cell Tot.Acid C.E.	Consistency Ratio* $(NaOH:H_2SO_4)eq$
I. Cell System Evaluation Period																
12	10/1/73	2.6N	753	99.6	675	89.3	1.52	92%	1.40	95%	.38	28%	1.96	-	-	1.12
13	10/5	2.4N	756	100.0	675	89.3	1.61	91%	.91	97%	.51	40%	1.88	36%	76% (c)	1.01
14	10/11	[illegible]	747	98.8	663	87.7	1.90	93%	.91	99% (a)	.40	30%	1.85	-	-	1.08
15	10/30	3.2N	756	100.0	672	88.9	1.89	89%	.96	92% (b)	.54	32%	2.03	41%	73% (c)	1.03
16	11/6	3.1N	915	121.	816	107.9	2.17	91%	1.55	93% (b)	.34	22%	2.16	58%	80% (c)	1.03
17	11/16	3.0N	750	99.2	669	88.5	2.02	89%	1.25	90%	.50	41%	2.02	35%	76% (c)	1.04
18	11/24	3.1N	756	100.0	672	88.9	1.69	86%	1.31	89% (a)	.59	53%	1.88	21%	74% (c)	1.03
19	12/19	4.0N	1074	142	963	127	2.02	91%	1.36	93%	.74	54%	2.24	34%	88%	0.99
20	1/2/74	3.0N	915	121.0	919	108.3	1.97	86%	1.15	91%	.46	19%	1.98	62%	81%	1.01
21	1/7	3.1N	912	120.6	813	107.5	1.94	87%	1.13	89%	.64	36%	2.11	49%	85%	0.99
								Av.= 90%		Av.= 93%						
22	1/23	4.2N	915	121.0	939	124.2	1.93	75%	.87	84%	.71	41%	2.10	38%	79%	0.91
23	2/4	3.8N	750	99.2	666	88.1	1.87	81%	1.02	86%	.48	17%	2.13	58%	75%	0.99
24	2/9	4.0N	909	120.2	819	108.3	1.95	80%	1.26	78%	.44	19%	2.01	64%	83%	1.00
25	2/12	3.6N	756	100.0	672	88.9	1.99	81%	1.05	83%	.50	24%	2.11	63%	87%	0.96
26	2/13	3.7N	753	99.6	669	88.5	2.04	79%	1.04	83%	.49	29%	2.05	55%	84%	0.95
27	2/26	3.8N	915	121.0	831	109.9	1.99	84%	1.11	90%	.45	29%	2.06	51%	80%	0.98
28	3/2	3.6N	1074	142	960	127	1.87	72%	.87	75%	.57	37%	1.95	32%	63%	0.99
29	3/6	3.7N	1074	142	813	107.5	2.14	73%	.79	69%	.67	43%	2.06	39%	82%	1.00
30	3/10	3.1N	1077	142.5	816	107.9	1.95	80%	.88	78%	.69	39%	1.92	39%	77%	1.03
31	3/16	3.2N	1074	142.1	960	127.0	1.91	74%	.75	72%	.56	27%	1.60	50%	77%	1.00
32	3/25	3.5N	912	120.6	810	107.1	1.84	63%	.75	62%	.60	42%	1.50	35%	77%	1.04
								Av.= 83%		Tot.Av=85%		Tot.Av=33%		Tot.Av=45%	Tot.Av=79%	
II. Advanced Component Evaluation Period																
33	4/11/74	3.5N	753	99.6	672	88.9	1.73	91%	1.35	89%	.67	46%	2.00	47%	93%	1.00
34	4/15	3.4N	756	100.0	681	90.1	1.89	91%	.98	93%	.48	54%	1.99	43%	97%	.97
35	4/30	3.5N	1052	139.3	792	104.8	1.95	91%	1.02	88%	.45	53%	1.91	45%	98%	1.00
								Tot. Av. 91%		Av.= 90%		Av.=51%		Av.= 45%	Av.=96%	

* Ratio of total equivalents of NaOH and H_2SO_4 involved in the C.E. Measurement.

(a) Accumulation term assumed negligible due to "2nd sample" titration inconsistency.
(b) Probable, although uncertain, result - due to inconsistency of one of three sample titrations.
(c) Slight external leakage of B-Anolyte occurred in these runs (see text).

In the last two-and-a-half months of the period (C.E. Nos. 22-32), the catholyte current efficiencies were all significantly lower. The deterioration of the cells was caused by crystallization as a result of too high a Na2SO4 feed concentration, i.e., in the vicinity 4N Na2SO4. This high concentration was first used for an extended period starting in mid-January. In the concentration ranges encountered, the crystallization point of the Na2SO4 -NaOH catholyte mixture decreases with increasing Na2SO4 concentration. However, crystallization occurs in this case when the temperature exceeds the crystallization point. As a result, localized crystallization occurred within the cells, specifically in the catholyte compartment, the mid-catholyte compartment, and extending into the cation membrane. The crystallized material was still present in five of eight "B" cells that were disassembled in late January to investigate unaccountably high voltages for that electric module.

It is noteworthy, based on the results obtained before crystallization occurred, that the current efficiency is independent of the current density, or production level, at least over the range covered, which is 70 percent, 85 percent, and 100 percent of design point.

As stated above, the combined catholyte current efficiency gives the performance of both the "A" and "B" cells together. The "A" anolyte current efficiency measures the "A" cells alone.* Table 6.4 indicates an average "A" anolyte current efficiency of 93 percent for the period before crystallization occurred, significantly exceeding the design basis of 85 percent. Current efficiencies were considerably lower after crystallization had occurred, indicating significant internal crossleaking.

The sulfuric acid produced in the "B" cells is divided between the "B" anolyte stream, which is essentially free of sodium (Figure 6.30, Stream 7), and the mid-anolyte stream, which contains sodium sulfate (Figure 6.30, Stream 10). This mid-anolyte stream is combined with the "A" anolyte product, which also contains sodium sulfate, and flows to the "front end" of the pilot plant for recycle to the stripper.

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*Note: The independently measured catholyte and anolyte current efficiencies must be equal for a given cell provided there are no undesirable side reactions at the electrodes and no external leakage of either product. Our prior experience with these cells indicates that the catholyte current efficiency may run slightly higher than the anolyte current efficiency.

The current efficiencies of the "B" anolyte and mid-anolyte are measured separately and are given in Table 6.4. The sum of these two efficiencies gives the current efficiency of the total acid produced in the "B" cells, also given in Table 6.4.

Of the results obtained before crystallization occurred, Table 6.4 shows that the "B" cell total acid current efficiencies are significantly below those of the combined catholytes in C.E. Nos. 13, 15–18. This suggests leakage of some acid from the system to the outside. The amount of leakage can be estimated by assuming an 85 percent overall current efficiency for the "B" cells. On this basis, the indicated leak rate for the "worst case" is 1.6 GPH (100 cc/min) of "B" anolyte acid. Leakage in the "B" anolyte recirculation pump (into the mechanical seal cooling water) was discovered in early December; new seals were installed by mid-month. C.E. No. 19 data were taken after the pump was rebuilt, and the "B" cell total acid current efficiency of 88 percent (Table 6.4 is consistent with the current efficiencies of the combined catholytes and "A" anolyte for that run, indicating no further external leakage. (Note: The design point throughput of the anolyte recirculation pump is 9.01 gpm so that even at 70 percent of design point, the 1.6 GPH leak rate was about 0.4 percent of the pump throughput.)

The two columns of current efficiencies for the "B" anolyte and mid-anolyte in Table 6.4 show wide scatter. However, where the mid-anolyte current efficiencies are high (C.E. Nos. 18 and 19), the "B" anolyte current efficiencies are low; and vice versa (C.E. Nos. 16 and 20.) Furthermore, where the mid-anolyte efficiency is high, the mid-anolyte acid normality is high; and where the mid-anolyte efficiency is low, the acid normality is low. These characteristics indicate the presence of an internal crossleak between the mid-anolyte and the "B" anolyte streams. The crossleak has been in one direction in some cases (e.g., C.E. No. 16) and the other in other cases (C.E. Nos. 18 and 19), depending on the relative pressures.

For C.E. Nos. 33–35, Table 6.4 shows little scatter for the "B" anolyte and mid-anolyte current efficiencies. Average values of 45 percent and 51 percent, respectively, were obtained in the absence of internal crossleaks. These exceed the design basis of 40 percent and 45 percent, respectively.

6.4.5.2 Energy Consumption Results - The total d-c energy applied to the bus bars for both the "A" and "B" cells divided by the total production rate of caustic by the two types of cells gives the overall specific energy consumption for caustic production, KWH/lb NaOH. Specific energy consumption results for both the "Cell System Evaluation Period" and the "Advanced Component Evaluation Period" are summarized in Table 6.5.

The "Performance Objective" values in Table 6.4 for the overall NaOH energy factors are based on the Phase I performance objectives (3N Na_2SO_4 feed solution, 140 F operating temperature, 85 percent NaOH current efficiency) but adjusted downward to reflect the actual current densities. The adjustment was made in accordance with the cell voltage-current density relationship given in Figure 6.31.

The "Measured" overall NaOH energy factors in Table 6.11 are calculated from the measured caustic production rates from both types of cells, the d-c bus bar current and the "Average Cell Voltage Excluding Highest E.M." (see Table 6.5). The latter is derived by subtracting the voltage of the electric module (eight cells in parallel electrically per electric module, Table 6.3) having the highest voltage from the bus bar voltages and dividing the result by the number of remaining electric modules. This was done to eliminate the effects of incomplete gas venting from the center compartment and/or mid-catholyte compartment of the pilot size cells. Table 6.5 contains both the average cell voltage with all E.M.'s and the "Average Cell Voltage Excluding Highest E.M." The latter are also given in Table 6.6 arranged in accordance with the Na_2SO_4 feed concentration and current density.

Table 6.5 shows that during the three-and-a-half months prior to the occurrence of crystallization in the cells (i.e., up to and including C.E. No. 21), the overall NaOH energy factors met the performance objectives at each production level. At the 70 percent production level (C.E. Nos. 12-15, 17, and 18), the overall NaOH energy factors matched performance objectives. For the 85 percent production level case (C.E. No. 16, 20, and 21), the measured energy factors "bettered" the performance objective by three percent. Finally, for the 100 percent production level case (C.E. No. 19), the measured energy factor "bettered" the performance objective by almost nine percent.

6.4.6 Advanced Component Evaluation Period

Because of the deterioration of the cells due to crystallization, the cells were rebuilt and some advanced components were installed. In particular, fluorocarbon based cation membranes were installed in most cells. Eight of these membranes had been installed as test specimens at the end of the "Initial Cell System and Process Debugging

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Table 6.5

SUMMARY OF VOLTAGE-CURRENT DATA AND SPECIFIC ENERGY CONSUMPTION RESULTS IN WEPCO PILOT PLANT CELL SYSTEM

				A - CELLS					B - CELLS					Overall NaOH [illegible] Factors	
							Av. Cell Voltage					Av. Cell Voltage			
C.E. No.	No. of Operating A/B Cells	Na_2SO_4 Feed Conc.	Av. Temp. °F	Busbar Current amps	Current Density ASF	Busbar Voltage volts	All E.M. volts	Excluding Highest E.M.'s volts	Busbar Current amps	Current Density ASF	Busbar Voltage volts	All E.M.s volts	Excluding Highest E.M. volts	Measured^d KwH lb NaOH	Performance Objective^e KwH lb NaOH
I. Cell System Evaluation Period															
12	[illegible]	[illegible]	140	753	99.6	41.5	5.93	5.90	675	89.3	23.5	5.87	5.87	1.95	2.21
13	[illegible]	[illegible]	133	[illegible]	100.0	42.0	6.00	5.98	675	89.3	23.5	5.87	[illegible]	[illegible]	2.21
14	56/32	[illegible]	139	747	98.9	42.0	6.00	6.00	663	87.7	24.8	6.20	6.13	1.97	1.99
15	[illegible]	[illegible]	[illegible]	[illegible]	100.0	41.3	5.90	5.88	672	88.9	24.0	6.00	[illegible]	[illegible]	2.22
16	[illegible]	[illegible]	132	915	121.0	43.0	6.14	6.12	816	107.9	26.0	6.50	6.50	2.29	2.19
17	[illegible]	[illegible]	141	750	99.2	42.4	6.06	5.93	669	88.5	26.7	6.67	6.50	2.10	2.20
18	56/32	[illegible]	136	755	100.0	39.5	5.64	5.47	672	88.9	23.8	5.95	[illegible]	[illegible]	2.21
19	[illegible]	[illegible]	141	1074	142.1	45.0	6.43	6.20	963	127.4	27.0	6.75	6.60	2.13	[illegible]
20	56/32	[illegible]	140	915	121.0	43.8	6.26	5.97	819	108.3	25.8	6.45	6.40	2.11	2.18
21	[illegible]	[illegible]	140	912	120.6	43.0	6.14	5.98	813	107.5	25.0	6.25	6.23	2.12	[illegible]
22	40^a/32	[illegible]	140	915	121,161	36.5	6.04,6.30	5.92,6.30	939	124.2	30.5	7.62	[illegible]	[illegible]	[illegible]
23	[illegible]	[illegible]	137	750	99.2	39.9	5.70	5.62	666	88.1	23.9	5.97	[illegible]	2.14	[illegible]
24	[illegible]	[illegible]	140	999	120.2	42.4	6.06	5.96	819	108.3	25.8	6.45	6.43	2.33	2.29
25	[illegible]	[illegible]	136	756	100.0	39.7	5.67	5.61	672	88.9	23.5	5.87	5.83	2.12	2.21
26	[illegible]	[illegible]	136	753	99.6	39.5	5.64	5.58	669	88.5	24.0	6.00	[illegible]	[illegible]	2.31
27	56/32	[illegible]	139	915	121.0	42.8	6.11	6.03	811	109.9	26.4	6.60	[illegible]	2.24	[illegible]
28	[illegible]	[illegible]	139	1074	142.1	47.5	6.79	6.59	960	127.0	28.0	7.00	[illegible]	2.93	[illegible]
29	[illegible]	[illegible]	[illegible]	1074	142.1	47.5	6.79	6.53	813	107.5	26.0	6.50	6.47	2.70	[illegible]
30	56/32	[illegible]	139	1077	142.5	47.2	6.74	6.47	816	107.9	26.0	6.50	6.43	2.44	[illegible]
31	[illegible]	[illegible]	[illegible]	1074	142.1	45.3	6.47	6.42	960	127.0	30.0	7.50	7.45	[illegible]	2.35
32	24^a/32	[illegible]	141	912	121,161	40.5	5.62,6.80	5.58,6.80	810	107.1	26.2	6.55	6.53	2.64	[illegible]
II. Advanced Component Evaluation Period															
33	[illegible]	[illegible]	[illegible]	753	99.6	39.3	5.72,4.95^c	5.72,4.95	672	88.9	23.4	6.15,4.95^c	6.10,4.95	1.91	2.21
34	[illegible]	3.62	[illegible]	756	100.0	39.0	5.62,5.25^c	5.61,5.25	681	90.1	23.7	6.23,5.00^c	[illegible]	[illegible]	[illegible]
35	[illegible]/24^b	[illegible]	[illegible]	1053	139.3	38.0	6.33	6.33	792	104.8	19.1	6.37	6.35	2.12	2.26

a. All 56 A-cells operating hydraulically

b. All 32 B-cells operating hydraulically.

c. Voltage of one electric module having "inert" anodes.

d. Calculated from measured caustic production rate, DC busbar current and average cell voltage excluding highest E.M.

e. Phase I Performance Objectives (3% Na_2SO_4 feed solution, 140°F, 85% NaOH current efficiency) but adjusted downward in accordance with the cell voltage-current density relationship given in Fig. 4 to account for the above actual current densities.

Period." Four of the eight were reinstalled after visual examination. The other four were analyzed and found to be in excellent condition despite some adverse conditions that had occurred during the nearly 2100 operating hours.

In addition, one electric module of "A" cells and one electric module of "B" cells were outfitted with "inert" anodes. These anodes have a coating of noble metal or noble metal oxides on a titanium substrate. They offer the potential of significantly lower voltage (see below), are free of corrosion products, and are dimensionally stable.

Aside from these cation membranes and inert anodes, new diaphragms and anion membranes of the same types as before were installed. Most of the lead alloy anodes and the cathodes were reused.

During the "Advanced Component Evaluation Period," the "A" and "B" cells operated for 885 hours and 889.5 hours, respectively. Operation of the pilot plant during the second half of this period was conducted with little contractor supervision to determine the operability of the SO2 removal plant by power plant operators. A continuous run of 412 hours, or 17.2 days, was made. This was not only the last run but also the longest uninterrupted run of the entire test program. The run had to be terminated due to failure of the acid sulfate pump, (P-104), which fed the mixed acid to the stripper.

6.4.6.1 Current Efficiency Results – Three current efficiency measurements were made during the first month of the period before the reduction in contractor personnel. The results are included in Table 6.4. The catholyte current efficiency, which gives the overall performance of the cells, was 91 percent, exceeding the design value of 85 percent.

The "A" anolyte current efficiencies averaged 90 percent and the "B" cell total acid current efficiency averaged 96 percent, both above design values. The "B" cell total acid current efficiency consists of the "B" mid-anolyte current efficiency of 51 percent and the "B" anolyte current efficiency of 45 percent (Table 6.3).

6.4.6.2 Energy Consumption Results - Energy consumption results for the Advanced Component Evaluation Period appear in Table 6.5, and cell voltages for the electric modules with "inert" anodes are summarized at the bottom of Table 6.6.

Table 6.5 shows that the overall NaOH energy factors for C.E. Nos. 33–35 are well within the performance objectives in each case.

Substantial voltage reductions with the "inert" anodes were realized as shown in Table 6.6, and can be more than

Table 6.6

SUMMARY OF "A" AND "B" CELL CURRENT-VOLTAGE DATA

Anode Type	Na_2SO_4 Feed Conc.	"A" Cells Current Density ASF	"A" Cells C.E. No.	"A" Cells Cell Voltage* volts		"B" Cells Current Density	"B" Cells C.E. No.	"B" Cells Cell Voltage*	
Pb alloy	2.4-2.6 N	100	(12)	5.90	5.94	89	(12)	5.87	5.85
			(13)	5.98			(13)	5.83	
	2.9-3.2 N	100	(14)	6.00	5.82	89	(14)	6.13	6.11
			(15)	5.88			(15)	5.90	
			(17)	5.93			(17)	6.50	
			(18)	5.47			(18)	5.92	
		121	(16)	6.12	6.02	108	(16)	6.50	6.39
			(20)	5.97			(20)	6.40	
			(21)	5.98			(21)	6.23	
							(30)	6.43	
		142	(30)	6.47	6.44	127	(31)	7.45	
			(31)	6.42					
	3.4-3.7 N	100	(33)	5.72	5.66	90	(33)	6.10	6.15
			(34)	5.61			(34)	6.20	
		121	(32)	5.58		107	(29)	6.47	6.45
							(32)	6.53	
							(35)	6.35	
		141	(28)	6.58	6.48	127	(28)	6.97	
			(29)	6.53					
			(35)	6.33					
		161	(32)	6.80					
	3.8-4.2 N	100	(23)	5.62	5.60	89	(23)	5.95	5.92
			(25)	5.61			(25)	5.83	
			(26)	5.58			(26)	5.97	
		121	(22)	5.92	5.97	109	(24)	6.43	6.50
			(24)	5.96			(27)	6.57	
			(27)	6.03					
		142	(19)	6.20		126	(19)	6.60	6.56
							(22)	6.53	
		161	(22)	6.30					
"Inert"	3.4-3.5 N	100	(33)	4.95	4.94	90	(33)	4.95	4.97
			(4/12)	4.75			(34)	5.00	
			(4/13)	4.80					
			(34)	5.25					
						163	(4/26)	5.4	

* Average cell (Electric Module) voltage excluding one E.M. with highest voltage (see Table III). The averages, therefore, are generally based on six E.M. voltage for A cells and three E.M. voltages for B cells. Voltage data for cells with "inert" anodes are for a single electric module.

25 percent at the higher current densities. At 160 ASF, the cost of electrical energy for the 75 MW prototype plant (3100 lb of SO_2 absorbed/hr) is reduced by approximately $60,000/yr (at $0.00781/kW) by using inert anodes. The incremental capital cost of inert anodes is not a significant part of the prototype plant costs.

6.5 PROCESS MATERIAL BALANCES

6.5.1 Process Losses

The mechanical loss of water and process fluids, sometimes totaling hundreds of gallons per day, occurred during the life of the pilot plant program and caused operating limitations. These losses were related to mechanical and handling problems. The sodium losses monitored in these streams accounted for all the make-up sodium required; therefore, make-up liquids were not required due to process problems. In addition to operating losses, shutdowns of more than a few hours required that the equipment be drained completely in order to avoid crystallization and plugging. These conditions represented a significant economic penalty and emphasized the need for careful loss monitoring and recovery facilities.

During the first several months of operation, several types of losses were identified and corrected. They were:

1. Absorber entrainment loss - corrected by using the third packing stage as a demister.
2. Entrainment from catholyte circulation tank—caustic loss controlled by lowering liquid level in separation tank.
3. Cell area pump seals - stopped by replacing pump seals with double mechanical seals and monitoring flush water for seal leakage.
4. External cell leaks - corrected by collecting and returning liquids to process.

6.5.2 Loss Analysis Run Results

During January, 1974, the absorption-stripping section and the cell room were operated separately for a period of 22 hours in an attempt to identify and quantify liquor losses from the system. This test was conducted after the electrolytic cells had been damaged by internal crystallization due to operation at high Na_2SO_4 concentrations in the cell feed liquor (see Section 6.6).

The main results obtained from this test were:

1. Pump drippings, samples, and miscellaneous losses in the absorption-stripping section amounted to 28.2 gal per day, representing a sodium loss of 580 gm-ion per day and a sulfate loss of 190 gm-ion per day.

2. The sodium inventory for the adsorption-stripping section (front end) remained constant, indicating no chemical losses other than that attributable to 1 above. Simultaneously, the sulfate inventory increased at a rate equivalent to 16.8% oxidation in the absorber. The observed sodium sulfate increase in the cell feed tank and the calculated sodium sulfate increase agreed within experimental error.

3. The water loss for the front end was 65 gallons per day or 540-pounds per day. This increased salt concentration in the cell liquor from 20.24 to 21.37 wt%. The maximum probable error was approximately 200 pounds of water per day.

4. Miscellaneous losses in the cell area were 7.5 gallons per day, representing a sodium loss of 80 gm-ion per day and a sulfate loss of 47 gm-ion per day.

5. The sodium and sulfate inventories for the cell area remained constant during the test indicating no chemical losses other than accounted for in 4 above.

6. The water disappearance in cell area amounted to 175 gallons per day: 11.8 percent due to electrolysis, 49.7 percent for humidification of the effluent O_2 and H_2 streams, 4.1 percent due to leakage, and the remaining 34.4 percent (or 60 gallons) could not be accounted for.

6.5.3 Discussion Of Results

Near the end of the test program, EPA carried out a series of tests on the absorption tower to determine the water content of the effluent gas and the entrainment of process fluids was determined. The flue gas rate and absorber temperature profile were essentially identical to those existing during the Loss of Analysis run. It was therefore assumed that similar losses existed in both cases. The comparative operating conditions and the measured losses are presented in Table 6.7.

6.5.3.1 Chemical Losses - Pump drippings and miscellaneous losses were the only chemical losses in the front end. Assuming a cell feed rate of 2.0 GPM, these losses were calculated to be less than 1% of the total fluid processed. The closure of the sodium balance indicated no extraneous leaks, such as continued absorber carryover. This was confirmed by the EPA study. An entrainment of 0.004 grains/SCF as sulfate ion corresponded to

TABLE 6.7

COMPARATIVE OPERATING CONDITIONS AND MEASURED LOSSES

	Gas rate (lb/hr)	TEMPERATURES (F) inlet	quench	outlet	SO2 removed (lb/hr)
Loss Analysis Run	5310	280	120	110	24.0
EPA Study	5544	270	120	105	33.3

	Stripper Overhead temperature (F)	Flue gas outlet % moisture	Front end Water loss (gal/day)	Entrainment grains/SCF as SO4
Loss Analysis Study	83	NA	65	NA
EPA Study	110	7.0	NA	0.004

0.014 gallons per hour of process fluids: this was only 0.05 percent of the net absorber flow and accounted for virtually no chemical losses.

The chemical losses in this test run were, therefore, due to the various leakages. They amounted to about 660 gm-ions of sodium per day or the equivalent of 62 gallons of cell feed liquor per day. During the test program substantial chemical losses did exist. In addition to leakage, other sources of chemical loss were absorber carryover and sodium lost via the "B" cell anolyte purge stream. The absorber carryover was corrected by using the third packing stage as a demister. Losses via the "B" cell anolyte were a result of cross leaks through the anion membrane caused by liquor crystallization and operational upsets. Measured values of Na in this stream were as high as 13,000 mg/l which at design flow rates would represent a sodium loss of 308 gm-ion per day. Replacement of the anion membranes late in the test program corrected this loss.

Not included in the analyses above were substantial liquor losses incurred by system drainage upon shutdown and losses resulting from operational errors. The shutdown losses amounted to as much as 100 gallons per shutdown when ambient conditions necessitated complete drainage.

6.5.3.2 Water Balance - The water balance for the process indicated a loss of 65 gallons per day from the front end and 175 gallons per day for the cell area. Water could be lost through carryover in the absorption tower, with the SO2 in the stripper overhead flow, by electrolysis within the cells and by humidification of the cell vent streams.

Based on the stripper overhead temperature and the SO2 removed during the Loss Analysis run, the water loss with the SO2 would be 3.2 gallons per day. The corresponding equilibrium SO2 concentration would be 98.4 wt%. A catch pot was installed in the stripper overhead line, but no substantial amount of water was collected. This indicated that entrainment of condensed water was minimal.

The water balance around the absorber was more complicated. The flue gas from the boiler, containing some water, entered the quench section at a temperature between 270 F and 310 F. It was cooled by water evaporation to 120 F and passed through a demister to the absorption section. The water pickup in the quench section was a function of gas flow, flue gas temperature, and inlet humidity. The gas passed through the absorbing stages at near quench temperature, but was cooled in the demisting (third) stage to about 105 F at the absorber outlet. This cooling appeared to be a result of heat losses to the atmosphere.

The EPA study indicated that the outlet gas contained 7% moisture as entrained water. This corresponded to water entrainment of 0.0017 lb H20/SCF dry gas or 305 gallons per day for the test. The water condensed in the third stage, assuming a temperature drop from 120 F to 105 F and saturated gas leaving the absorber, was 0.0021 lb H20 SCF dry gas or 369 gallons per day. Thus it appeared that the majority of the condensed water was carried overhead. Depending upon the exact temperature profile across the third stage, the effective height of packing was reduced and demister efficiency decreased correspondingly.

Based on the above, the process liquor inventory should have shown a net water gain of about 64 gallons per day if the flue gas was saturated at 120 F as it left the quench section. However, with a water loss in the absorber of 61.8 gallons per day for the 22 hour Loss Analysis run, the relative humidity of the flue gas leaving the quench section was calculated to be 90 percent. This would result in a water evaporation in the chemical section of 0.00071 lb H20/SCF dry gas or 124 gallons per day and close the system water balance. If the holdup in the absorber and the net throughput are assumed to be 60 gallons and 30 gallons per hour respectively, a loss of 61.8 gallons per day from a 20 percent salt solution will concentrate the net draw solution by 7%. This concentration increase is comparable to that measured by sodium balances through the tower. During the Loss Analyses run, the ratio of total Na^+ in the caustic feed to total Na^+ in the net draw was 1.06 to 1.08. This shows excellent agreement with the concentrating effect predicted by assuming that the inlet gas was not saturated.

The humidity of the inlet flue gas could not be measured during the test program. However, a boiler manufacturer's efficiency figures indicated the water content of the inlet flue gas might be 0.0504 lb H20/lb dry gas. This was based on an unknown moisture and hydrogen content in the coal. With that inlet humidity and a quench section effluent humidity of 90%, the water pickup in the quench would be 0.00193 lb H20/SCF dry gas. This estimate does not check with the adiabatic saturation temperature of 120 F. The heat balance will be satisfied only if there is 0.0372 lb H20/lb dry gas in the inlet gas. Flue gas humidity at this level can result from the combustion of coals with hydrogen and moisture contents of approximately 2.7 and 8.3 percent respectively. These values are not typical and lower inlet humidity was apparently closer to the correct value for this test run.

Water loss via electrolysis in the cell area was estimated to be about 20 gallons of water per day. This loss was calculated from the cell amperage measured for the Loss Analysis run. This value varied with particular operating levels for the test program.

The water loss by humidification of the O2 and H2 vent streams from the cells was calculated from the difference in humidity between the vent streams and the ambient air used for dilution and the CFM ratings of the cell dilution air fans. No attempt was made to measure the actual gas flow rates of these vent streams. Water loss by this humidification was estimated to be 87 gallons per day.

The balance of the water loss, 60 gallons per day, was unaccounted for.

During the last months of the test program, water was added to the cell feed liquor tank to maintain a constant density feed to the cells. This water was added at a rate dependent upon hourly hydrometer readings and averaged about 60 gallons per day. This was lower than the expected 230 gallons per day measured during the Loss Analysis run. Changes in inlet flue gas water content, ambient humidity, as well as varying levels in the cell system surge tanks could well account for these differences. Additionally, slight density changes, undetectable with a hydrometer, could have resulted in a difference of several hundred gallons of water in the 4000 gallon tank. Continuous operation was not maintained long enough (the longest run being nine days) to permit resolution of these differences.

6.6 CELL FEED TREATMENT

The feed to the electrolytic cells should be free of substances which will cause operational difficulties. Examples of such substances are calcium carbonate and iron, aluminum and magnesium hydroxides which will themselves, or after reaction in the cell environment, form materials which will settle out in the cells or be filtered out by the microporous diaphragms. The cell feed should also be relatively free of substances which will deleteriously interact with cell components. An example is chloride, which at high concentrations reduces the useful life of lead alloy anodes. There is an economic trade-off between keeping such substances out of the cell feed (by selection of suitable materials of construction or by selection of chemicals for feed liquor makeup, for example) and removing the substances from the feed. At the beginning of the pilot program, a tentative cell feed specification was formulated based on experience with other electrochemical systems. This specification is summarized in Table 6.8. The table also lists the present specifications based on experience with the pilot plant.

6.6.1 Contaminant Removal

In the initial pilot plant design, the acidic stripper drum effluent was cooled to about 130 F and sent to the cell feed liquor tank. There was some pH buffering in the stripper drum but the bulk pH control was by caustic addition directly to the feed tank. Poor mixing in the feed tank and the lack of continuous pH monitoring made control very difficult. This resulted in large pH fluctuations and excessive caustic consumption. The recycle caustic requirement for pH control has an effect on the plant economics since it increases the overall NaOH/SO2 ratio and, hence, the number of cells. The cell feed liquor was then filtered for bulk iron removal as the hydrous metal oxide passed through a manganese zeolite filter for ferrous iron removal and sent to the cell system feed tank.

TABLE 6.8

CELL FEED SPECIFICATION

	Tentative Feed Specification (PPM)	Present Recommendation (PPM)
Fe	< 0.1	< 0.5
Mn	< 0.5	< 0.5
Ni	< 0.5	< 0.5
Cu	< 0.5	< 0.5
Co	< 0.5	< 0.5
Al	< 0.5	< 0.5
Ca	< 5.0	< 15
Mg	< 0.5	< 15
Si	< 12.0	< 12
Cl	< 100	< 200(1)

(1) with lead alloy anodes

An intermittently regenerated manganese zeolite filter consists of a bed of microporous natural or synthetic alumino-silicate ion exchange granules treated with manganous chloride to convert it to manganous zeolite. Intermittent treatment with or a continuous body feed of potassium permanganate results in the precipitation of higher oxides of manganese on the zeolite grains. Oxidation reactions occur between the ferrous iron content of the cell feed and the manganese oxides on the grains. Regeneration is required because the oxidizing capacity of the bed is consumed in the process of iron removal. The bed also functions as a filter media for the ferric hydroxide formed. Backwashing the precipitated iron from the bed is necessary. Filtration rate is about three gallons per square foot per minute and backwash rate a minimum of eight gallons per square foot per minute.

The pH of the feed tank was initially between 10 and 12 to maintain the caustic environment necessary for iron removal. Operation at a lower pH level was not controllable with the initial system. However, the electrolytic cells fouled fairly rapidly as a result of occasional upsets when the pH dropped below 7. The cell area polishing filters also required frequent changing during this period. The material on these filters was analyzed as the hydrous metal oxide of aluminum.

It was suspected that the aluminum was being leached from the aridsorb resin. Further investigation, in conjunction with the resin supplier, determined that at a pH of 11.6 or greater, aluminum was leached from the silica-alumina base.

It was recognized that the existing system could not effect control in the desired pH range, 8-9, and modifications were undertaken. A pH buffer tank with automatic pH control was installed and the manganese zeolite filter moved to a point between the cell feed tank and the cell area polishing filter. The manganese zeolite filter was still required for ferrous iron removal, but was moved downstream of both pH adjustments to prevent any upsets in its operation. An auxiliary caustic tank was also installed to provide an accurate measure (batchwise) of the recycle caustic requirements.

Over the next two months, the pilot plant was plagued with problems resulting from the poor performance of the manganese zeolite filter. The cause was traced to a combination of residual oxidizable materials in the cell feed liquor and high inlet temperatures which resulted from periodic operation of the cell system in isolation from the front end. The MnZe unit was designed for a feed of several parts per million ferrous iron. However, due to the several hundred parts per million SO3 which remained in the cell feed after stripping, the resin at times would saturate allowing break through of iron and release of manganese. In addition, operation of the unit with the temperature above 110 F broke down the resin. The situation was clouded for a time as a result of erroneous iron analyses being received due to interference from sodium sulfate with the atomic absorption method used. A wet chemical method based on orthophenanthroline was found to give satisfactory results without interference and was used thereafter for iron determinations (see Appendix G).

It was decided that the manganese zeolite filter was impractical for iron removal under these conditions; therefore, the oxidative function of the manganese zeolite was replaced with a continuous feed of hydrogen peroxide.

Following laboratory tests demonstrating that H2O2 satisfactorily oxidized Fe+2 to Fe+3 in strong sodium sulfate solutions containing residual sulfite, the method was applied to the pilot plant. Hydrogen peroxide was added to the process stream at the pH control point upstream of the large cell feed liquor tank.

For the initial evaluation in the pilot plant, H2O2 at a concentration of 23.5 percent was added at a conservative rate of 15.4 cc/min. This rate of addition is sufficient to oxidize stoichiometrically an SO2 concentration of 790 mg/l in the stripper bottoms stream at a flow rate of 1.8 gpm. Table 6.9 shows the effectiveness of the peroxide. Column 4 shows that good iron removal was accomplished throughout the period, even with two high excursions of SO2 in the stripper bottoms.

The amount of H2O2 that was added for the initial evaluation was clearly more than was necessary and was reduced in subsequent tests. For the period from 12/16 to 12/19, Table 6.9 shows an average SO2 concentration in the stripper bottoms of 294 mg/l, or 89 mg/l if the two high excursions on 12/18 are omitted. Therefore, the H2O2 addition rate averaged more than 2.5 times the stoichiometric amount based on 294 mg/l of SO2, or 9 times based on 89 mg/l of SO2.

Additional data for the first week in January is given in Table 6.10. All subsequent running was done with peroxide addition and with the MnZe unit removed from service. Satisfactorily low iron levels were consistently obtained in the cell feed at the stacks.

The conservative minimum amount of peroxide to be added for iron oxidation is that amount which will react stoichiometrically with the SO2 and Fe in the stripper bottoms. Over a nearly three-month period starting in mid-December, SO2 and Fe concentrations in the stripper

Table 6.9

PROFILES OF SO2 AND Fe IN FEED LIQUOR BETWEEN STRIPPER DRUM AND CELL STACKS DURING INITIAL RUNNING WITH "HEAVY" H2O2 ADDITION

		1		2		3		4	
		Stripper Bottoms (@ T-103 inlet)		Feed Tank Contents (@ R-103 suction)		Cell Feed @ HX-5 (Valve S-21)		Cell Feed @ Stacks (Valve S-20)	
DATE 1973	TIME	SO2 mg/l	Fe mg/l	SO2 mg/l	Fe mg/l	SO2 mg/l	Fe mg/l	SO2 mg/l	Fe mg/l
12-16	1300	-	-	nil	<0.01	-	-	-	-
12-16	1700	nil	6.00	nil	0.30	12.8	<0.01	nil	<0.01
12-16	2000	nil	6.50	nil	0.80	nil	<0.01	nil	<0.01
12-17	0000	80.0	6.00	nil	1.50	-	-	-	-
12-17	0400	12.8	0.45	nil	1.10	-	-	-	-
12-17	0800	262.4	5.0	92	1.00	nil	<0.01	nil	<0.01
12-17	1330	289	5.0	nil	1.20	nil	<0.01	nil	<0.01
12-17	1600	44.8	4.1	6.4	1.0	12.8	0.02	nil	<0.01
12-17	2000	153.6	4.1	nil	1.1	nil	0.02	nil	<0.01
12-18	0000	51.2	4.4	nil	0.90	25.6	<0.01	nil	<0.01
12-18	0400	2176	5.0	12.8	0.70	25.6	<0.01	12.8	<0.01
12-18	0800	25.6	4.8	25.6	0.71	12.8	<0.01	nil	<0.01
12-18	1200	1069	4.5	25.6	0.80	25.6	<0.01	nil	<0.01
12-18	1600	38.4	4.4	12.8	1.0	nil	-	nil	<0.01
12-18	2000	51.2	4.5	19.2	0.8	25.6	0.04	51.2	<0.01
12-19	0000	51.2	4.3	51.2	1.3	38.4	<0.01	19.2	<0.01
12-19	0400	121.6	4.4	12.8	1.3	12.8	<0.01	12.8	<0.01
12-19	1210	19.2	4.3	nil	1.3	-	-	-	-
12-19	2000	-	-	-	-	-	-	19.2	<0.01
12-23	2200	-	-	-	-	-	-	nil	<0.01
12-24	0800	-	-	-	-	-	-	45	<0.01
12-24	1200	21.6	4.8	15.0	4.7	-	-	-	-
12-24	2200	-	-	-	-	-	-	8.3	<0.01

NOTES:
(1) Stripper bottoms flow @ 1.8 GPM (pH2) throughout the period.
(2) H2O2 added between Cols. 1 and 2 at 15.4 cc/min, 23.5% H2O2.
(3) G-103 filter between Cols. 2 and 3.
(4) CF 1/3 (or 2/4) filters between Cols. 3 and 4.
(5) MnZe Conditioner G-105 by-passed throughout the period
(6) Minimum detectable limit of "SO2" analysis is 12.8 mg/l.
(7) Fe analysis by orthophenanthroline method, by WAPCO lab.

TABLE 6.10

SO2 and Fe PROFILES IN MAJOR STREAMS OF WEPCO PILOT PLANT

Date	Time	1 Stripper Bottoms (@ T-103 Inlet) SO2		2 Feed Tank Contents (@ P-103 Suction) SO2		3 Cell Feed at Stacks (Valve S-20) SO2		4 Caustic Recycle Drum (M-105) (@ P-105 Suction) Fe	5 Acid Sulfate Recycle Drum (M-104) (@ P-104 Suction) Fe	6 Absorber Net Draw (@M-103A Outlet) Fe
			Fe		Fe		Fe			
1974		mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
1-2	1600							1.0	<0.01	
1-2	2200					nil	<0.01			
1-3	0800					nil	<0.01			
1-3	1200	nil	4.4	14.9	1.8					0.70
1-3	1600							0.36		
1-3	2200					41.3	<0.01			
1-4	0800					nil	<0.01			
1-4	1200	51	4.6	nil	0.10					1.0
1-4	1600							0.60	<0.01	
1-4	2200	nil				nil	<0.01			
1-5	0800					nil	<0.01			
1-5	1200	nil	1.1	nil	0.60					0.29
1-5	1600							0.19	<0.01	
1-5	2200					nil	<0.01			
1-6	0800					nil	<0.01			
1-6	1200	nil	1.0	nil	1.7					0.31
1-6	1600							0.10	<0.01	
1-6	2200					nil	<0.01			
1-7	0800					-	<0.01			
1-7	1200	nil	2.5		1.5					0.60
1-7	1600							0.15	<0.01	
1-7	2200					38.4	<0.01			
1-8	0800					nil	<0.01			

NOTES:
(1) Stripper bottoms flow 1.35GPM
(2) H2O2 added between cols. 1 & 2 @ 7.1 cc/min, 22.5%
(3) Filters G-103 and CF 1/3 (or2/4) between Cols. 2 and 3.
(4) MnZe Conditioner G-105 by-passed throughout the period.
(5) Minimum detectable limit of SO2 analysis is 25 mg/l.
(6) Fe analysis by orthophenanthroline method, by WEPCO lab.

bottoms averaged 54 and 3.2 mg/l, respectively. The SO2 average is based on 43 analyses; it excludes four other analyses, three of which clearly indicate upset conditions and the fourth is during a response test. The Fe average is based on 35 analyses during the subject period.

6.6.2 Major Stream Analysis

Table F-4 in Appendix F presents a summary of the cations found in the major plant streams on several different occasions with the accompanying chemical analysis. A detailed discussion of one such set of analyses is presented in Appendix A. Several general comments can be made, however, concerning these analyses.

1. A comparison of sample 349 with sample 350 will show Mn leaching from the manganese zeolite filter.

2. The drop in the iron levels during the test program is indicative of the removal of corroding equipment, mainly in the stripper. The chromium analyses also are indicative of this trend.

3. Ca and Mg levels in the net draw are indicative of quench water carry-over into the chemical section. Samples 45, 64, and 246 are prior to the installation of the demister.

4. Na in the "B" anolyte was a result of leaks in the anion membrane and represents a process fluid loss. In cells free of cross leaks, sample 242, the sodium losses are negligible.

5. Chloride levels over 200 mg/l are deleterious to the anodes. The drop in the chloride levels reflect the use of mercury cell caustic as opposed to diaphragm cell caustic for feed makeup. Anode breakdown may be the cause of the Pb levels in the anolyte samples. During pilot plant operation, the chloride ion concentration did not build up to greater than 200 mg/l after mercury cell caustic was used for solution makeup. Since no chloride buildup was observed in the pilot plant, chloride introduced from the fuel gas was inconsequential.

6. Silica levels are indicative of fly ash dissolution in the process fluids.

7. Sodium can be used as a tracer for the relative mixing volumes of the plant streams. For example, "A" anolyte (45,000 mg/l) mixes with the absorber net draw (65,000 mg/l) to form cell feed liquor

(51,000 mg/l). Thus the relative volumes are 1 net draw plus 2.3 anolyte to form 3.3 feed liquor.

6.6.3 Sources of Metal Contaminants

The two primary sources of metals contamination are equipment corrosion and fly ash dissolution.

There was a significant amount of corrosion in the pilot plant especially during the earlier stages of operation. The most severely attacked piece of equipment was the stripper. The overhead spool piece on the outlet of the overhead condenser and the stripper bottoms piping were completely corroded and made a significant contribution to the iron contaminants. The carbon steel spool piece (installed by mistake) was later plastic coated and the stripper bottoms piping problem (a field fabrication error) was corrected. The iron levels dropped significantly after the repairs were completed. This can be seen in Table F-4 in Appendix F.

The detailed contribution of dissolved fly ash to the metals contaminants is not easily determined and can only be inferred. The efficiency of the hydroclone was not measured. While qualitatively there was more fly ash in the hydroclone bottoms, the ratio of the flow of quench and makeup water to the solids involved was so large that efficiency measurements were meaningless. This fact combined with insufficient data input on inlet fly ash quantity makes any calculation of fly ash entry to the chemical section of the absorber speculative. Furthermore, there is little data on the solubility of metals contained in the fly ash in the plant solutions.

At a precipitator efficiency of 98 percent, WEPCO estimates the dust loading to the absorber to be 0.04 grains per cubic foot of gas. Table 6.12 is an elemental breakdown of seven typical fly ash analyses.

At iron and aluminum levels based on sample 7 and the dust loading as above, the expected iron and aluminum hydroxide to be filtered from the cell feed liquor will be 1.31×10^{-6} and 1.91×10^{-6} lb/ft^3 gas. This assumes 100 percent of the fly ash enters the chemical section and the iron and aluminum are 100 percent dissolved. A typical boiler gas flow of 250,000 CFM should contribute no more than 1.96 and 2.86 lb/hr of iron and aluminum as hydroxides from the fly ash.

A sample of typical fly ash was sent to Commercial Testing and Engineering Company for analysis. Their results are shown in Table 6.11. The most significant number is the weight percent water soluble fraction. If the quench section removes 90 percent of the ash and only 2.1 percent of that left is soluble (the iron and aluminum are small fractions of the total solubility), the hydroxide loadings could be reduced by a factor of 500. Translating this into unit concentrations (mg/l) at the base case of 2000 CFM gas flow, an absorber net draw flow of 0.8 gpm, and the factor of 500 as derived above, the expected elemental iron and aluminum concentrations in the net draw would be 0.4 and 0.11 mg/l, respectively. This agrees quite well with what was actually measured in the net draw (see Table F-4 in Appendix F).

TABLE 6.11

TYPICAL FLY ASH ANALYSIS FROM WEPCO VALLEY PLANT*

Water Soluble (2.12% of total, dry basis)	Dry Basis (Wt. %)	Insoluble Residue (97.88% of total, dry basis)	Ignited (Wt. %)
Sulfate, SO_4	1.39	Phos. pentoxide, P_2O_5	0.15
Calcium, Ca	0.66	Silica, SiO	45.00
Sodium, Na	0.04	Ferric oxide, Fe_2O_3	24.83
Silicon, Si	0.01	Alumina, Al_2O_3	19.91
Aluminum, Al	0.01	Titania, TiO_2	1.08
	2.11	Lime, CaO	4.95
		Magnesia, MgO	0.99
		Sulfur trioxide, SO_3	0.21
		Potassium oxide K_2O	2.48
		Sodium oxide, Na_2O	0.36
		Undetermined	0.04
			100.00

*Carbonate carbon is 0.18% of total, dry basis; noncarbonate carbon is 2.05% of total, dry basis.

TABLE 6.12

ELEMENTAL BREAKDOWN OF SEVEN TYPICAL FLY ASHES (WEPCO DATA)
(Units are parts per million, ppm)

ELEMENT	1	2	3	4	5	6	7
S	4600	7600	15000	5500	12200	12700	3800
br	25	1	7.6	15	15	13	5.3
Cl	370	150	365	272	280	660	250
F	170	120	175	327	134	100	20
Al	86000	94000	72000	102000	73600	95500	116000
Sb	15	19	25	21	13.6	10.4	7.5
As	213	220	84	168	100	92	75
Ba	641	735	1900	637	657	644	877
Be	11.7	3.3	5.3	9.0	16.0	7.7	7.3
B	70	70	85	205	170	125	85
Cd	1.6	.80	1.0	2.0	1.6	1.25	.83
Ca	9900	12700	32800	16600	26000	43300	14340
Cr	219	178	191	174	165	179	178
Co	108	71	87	94	87	101	69
Cu	115	157	110	100	110	170	110
Fe	126000	147000	146000	166000	149000	103000	120000
Pb	275	301	269	586	158	222	237
Mg	9300	7600	10300	7100	8050	11460	9500
Mn	254	302	532	280	366	460	325
Hg	<.06	<.05	.18	<.14	.16	<.2	<.2
Mo	90	44	54	39	18	25	5
Ni	580	622	527	585	607	512	485
K	17200	17500	22800	17800	18500	13400	15500
Se	.24	5.0	.55	<.8	3.0	2.2	<.9
Ag	<.4	<.25	1.2	1.3	<.3	1.8	<.8
Na	6380	7410	13600	5120	6900	18300	3600
Tl	23	35	29	50	29	21	50
Sn	<9	51	26	56	92	<18	107
Ti	5700	4450	4000	5140	5900	6630	6300
Zn	200	163	215	189	218	222	200
V	296	310	427	304	256	276	320
I	<1.2	<3	<6	N.D.	267	6	1.

6.6.4 Cell Feed Liquor Conditioning in Future Installations

The cell feed liquor conditioning system in future plants will be designed to carry out the following processes:

1. Oxidation of ferrous iron at a level of 1 to 5 milligrams per liter of cell feed with hydrogen peroxide in the presence of about 50 milligrams per liter of sulfite.

2. At least one hour of ferric hydroxide conditioning after peroxide precipitation. This permits the ferric hydroxide gel particles to grow and/or coalesce. The rate of coalescence depends on the temperature, pH, concentration of iron, concentration of other insoluble substances, and presence of conditioning assistants. The rate of growth is maximum at high temperatures and, in the absence of other insoluble substances, at pH's near 5.5. If the concentration of iron is low (i.e., 1 milligram per liter or less) it may be desirable to add one or more milligrams/liter aluminum sulfate, sodium aluminate, or ferric sulfate or conditioning assistants to increase the rate of conditioning and improve subsequent filtration.

3. Precipitation of other heavy metal oxides and hydroxides (i.e., those of chromium, manganese, cobalt, nickel, and copper) and the oxides and hydroxides of silicon and aluminum by adjusting the pH of the cell feed to about 8.5. Such pH adjustment will be virtually simultaneous with the peroxide addition discussed above. Conditioning requirements are essentially the same as those for ferric hydroxide. The optimum pH for precipitation and conditioning depends upon the relative concentrations of the various insoluble metal oxides and hydroxides.

4. Precipitation of calcium as the carbonate. The carbonate required (about twice the concentration of calcium) is expected to be supplied from carbon dioxide (unavoidably) absorbed from the air into the cell feed liquor drum (cell feed surge tank) and the caustic recycle drum (effluent catholyte surge tank).

5. Removal of solids by precoat filtration using a diatomaceous earth precoat and body feed. Precoat requirements are estimated to be about 0.2 pounds (dry weight) per square foot of filter area. Body feed requirements are estimated to be about 0.3 pounds (dry weight) per thousand gallons of cell feed liquor. The 75 MW prototype plant would use 62 tons of diatomaceous earth annually. This would generate 124 tons of 50 percent wet cake annually or about 2.5 tons per week. The ash disposal rate from the boiler to be serviced by the prototype plant averages about 180 tons per week. The filter cake would increase the amount of solids by about 1.4 percent.

VII

DISCUSSION OF OPERATING RESULTS

7.1 PROCESS CONSISTENCY

In general, the majority of operational problems experienced during the pilot plant operation were mechanical. Examples of these problems were forced draft fan vibration and recycle acid pump failure. Table 7.1 presents a summary of the integrated pilot plant operation and availability. As the various mechanical problems were corrected, the operating frequency increased dramatically. High availability and low operating frequency during the later months was attributable to power plant boiler failure resulting in loss of flue gas to the unit. Appendix B presents a chronological history of all pilot plant operations from initial commissioning through later stages of operation. The test program encompassed the period from July 1973 to March 1974.

TABLE 7.1
PILOT PLANT OPERATION AND AVAILABILITY

	Total Hrs.	Hrs. Running	%	Hrs. Avail.	%
July, 1973	744	30	4.2	30	4.2
Aug., 1973	744	181	24.3	181	24.3
Sep., 1973	720	0	0	0	0
Oct., 1973	744	249	33.5	469	63.0
Nov., 1973	720	248	34.4	248	34.4
Dec., 1973	744	142	19.1	212	28.5
Jan., 1974	744	419	56.3	463	62.3
Feb., 1974	672	484	72.1	588	87.9
March, 1974	744	499	67.0	549	74.0
April, 1974	720	378	52.5	64.3	89.5

Since the electrochemical cells are the only basically new component in the overall SO2 removal process, it is worthwhile to break out the availability of the cells during the test program.

During the first three months of operation of the integrated pilot plant ("Initial Cell System and Process Debugging Period", see Sections 6.4.3 and 6.4.4) the cells were subjected to excessively abusive conditions stemming from the MnZe conditioner, in situ acid washes and excessive chloride levels. During this time, several shutdowns were made due to the cells or to cell-related causes for in situ acid washes, replacement of the bed in the MnZe unit, etc. At the end of the period, the cells were rebuilt with new membranes and diaphragms. Anodes and cathodes were reused.

After the cell rebuilding and for the remaining nine months of the test program, the availability of the elctrochemical cells was over 90%, as the following figures show:

Period: 2 October 73 to 29 June 74

Period Time	6,504 hours
Cell System Operating Time	2,978 hours
Down Time	
For cell maintenance	408 hours
For non-cell maintenance (i.e., FD fan vibration and bearings, pump seals, and shafts, recharging system chemicals, chemical system revisions, causes other than pilot plant, etc.)	3,048 hours
Unaccounted for	70 hours
Total Down-Time	3,526 hours

$$\text{Overall Cell System Service Factor} = \frac{2,978}{6,504}(100) = 45.8\%$$

$$\text{Cell System Availability Factor} = \frac{2,978 + 3,048}{6,504}(100) = 92.7\%$$

7.2 PROCESS CONTROL

The parameters of process control, including system response times and instrumentation design basis, are discussed below for the four major sections of the pilot plant: absorption, stripping, feed liquor preparation, and electrolytic cell operation.

7.2.1 Absorption

The caustic flow rate is the most important parameter in the absorption section. Insufficient caustic will result in lowered SO2 removal while excessive caustic will increase oxidation and decrease caustic efficiency. During the pilot plant operation, the caustic flow was controlled by monitoring the SO2 outlet concentration and the pH of the net draw. The net draw pH was a good indication of the relative sodium sulfite–sodium bisulfite concentrations (Figure 8.1). The system was normally operated at pH of 5.0 ± 0.2 which was easily maintained by hourly monitoring.

In later stages of the test program, the response of the absorber to step changes in SO2 inlet level and gas rate was measured. There were five specific tests performed. They are shown in Table 7.2 with their specific objectives. The results of the test are presented graphically as Figure 7.1. When control of the caustic flow was feed forward, based on SO2 inlet conditions and gas rate, the specified SO2 outlet concentration was maintained over a wide range of inlet gas conditions (Tests A, B, and E). When control of the caustic flow was by the SO2 outlet concentration, long response times due to the large absorber holdup were experienced (Tests C and D). Since such slow responses would result in periods during which SO2 outlet requirements could not be met, the more reliable feed forward control would be preferred for future installations.

Inaccuracies inherent in the measurement of large gas flows can be overcome with instrument tuning. Minor adjustments to attain a specific net draw pH or for slight variances in the outlet SO2 concentrations can be handled by the operator.

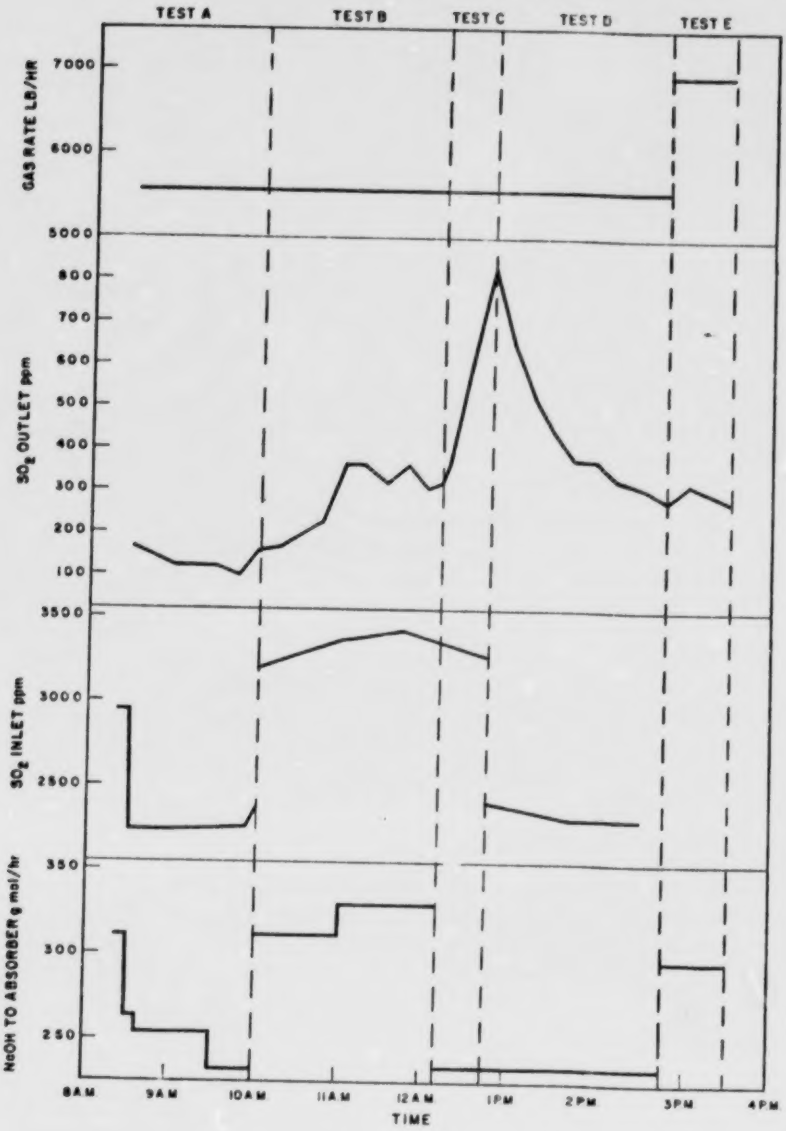

Figure 7.1 Absorption Tower Response Testing

TABLE 7.2

ABSORPTION TOWER RESPONSE TESTING

TEST	OPERATION	OBJECTIVE
A	Cut SO2 inlet and caustic flow simultaneously with gas flow constant.	Can system balance be maintained? SO2 outlet on specification?
B	Raise SO2 inlet and caustic flow simultaneously with gas flow constant.	As above.
C	Cut caustic flow with SO2 inlet and gas flow constant.	How rapidly will SO2 outlet exceed specification level?
D	Cut SO2 to correspond to lower caustic flow.	How rapidly will system recover?
E	Raise gas flow and caustic flow simultaneously with constant SO2 inlet.	Can system balance be maintained? SO2 outlet on specification?

7.2.2 Stripping

The rate of acid addition is a very important parameter in the process economics, as discussed in Section 6.3. The initial pilot plant pH control system required the withdrawal and pH measurement of a small slipstream at the base of the stripper. This control system failed as a result of inadequate winterizing. The acid addition was then controlled by hourly readings of the stripper drum outlet pH. Due to the large holdup time in the stripper drum, control of the acid addition was poor, but not impossible. However, as the stripper drum volume to feed rate ratio decreases, controllability will increase. A pH level of 4.0 should be attainable without elaborate neutralization according to the titration curve for sodium sulfate (Figure 6.27).

Steam flow to the reboiler is best set manually. Since SO2 removal is a strong function of the acid addtion, the steam rate is better set at a rate slightly above the anticipated minimum required with minor adjustments for ambient temperature added.

7.2.3 Feed Liquor Preparation

The pH neutralization system for the cell feed liquor was discussed in Section 6.6. The system as modified worked quite well.

Control of the feed liquor density is also important. Gradual salt concentration due to water loss will increase feed liquor density. However, if one monitors the density of the whole tank in order to control the water addition, the large volume of solution will mask density changes. The density should be monitored on the pH buffer tank effluent. Continuous control is not required but a density indicator for use with the water flowmeter is essential.

7.2.4 Cell Room

The cell room process control as described in previous sections functioned adequately.

7.3 MATERIALS OF CONSTRUCTION

As part of the test program, sample metal test coupons were placed in the various chemical environs of the process. After exposure, these coupons were removed and analyzed. The results of these analyses are presented in Table F-5 in Appendix F. The cell room materials of construction as determined in previous sections herein performed adequately.

7.4. EQUIPMENT OPERATING EXPERIENCE

7.4.1 SO2 Analyzer

The Intertech Uras analyzer performed quite well for the entire test program. Table 7.3 compares measured SO2 levels as determined by the Intertech analyzer, wet chemistry method (EPA), and the WEPCO Theta analyzer. The high end values determined by EPA and the Intertech agree quite closely, but the Intertech appears to be reading high at low SO2 levels. This may be due to nonlinearity in the I/P converter (the emf signal from the Intertech is coverted to a pressure signal for a chart recorder) as opposed to a bias in the Intertech. Periodic cleaning of the probes was required. Fly ash deposition and ice buildup (due to low ambient temperatures) restricted flow through the inlet and outlet probes, respectively. The probes can be cleaned on line and restricted gas flow is easily detectable. The plugging was apparently caused by the intermittent operation of the unit.

TABLE 7.3

COMPARATIVE SO2 MEASUREMENTS
(All Values In Parts Per Million)

EPA	INTERTECH	WEPCO
288	440	
352	472	
286	420	
322	300	
3130	3160	
3102	3080	
3160	3000	
	1275	1142
	39	18
*1894	1870	1779

* Calibration Gas

7.4.2 Flowmeters

The stripping column overhead flowmeter was inoperative for most of the test program due to obstructed impulse lines. It is believed that SO2 hydrate formation near the orifice taps was responsible. Impulse lines should be heat-traced and as short as possible.

The recycle acid flowmeter required frequent recalibration. This was necessary due to the attack of the acid sulfate solution on the differential pressure cell internals. The 316 SS internals were not satisfactory. The dp cell was filled with barometer fluid to eliminate contact with acid sulfate solution, but fluid losses from valve and fitting leaks made frequent recalibration necessary.

7.4.3 pH Meters

The stripper bottoms pH meter was inoperable for most of the winter months due to inadequate insulation and cooling water control. While operable, the Uniloc 320 held calibration and performed well, but the frequent sample line plugging made continued operation inconvenient.

7.4.4 Temperature and Pressure Indicators

The plastic protective coating of the thermowells was unsatisfactory. Nearly 90 percent of the thermowells failed due to corrosion after the plastic coating had split. Pressure indicators in stripper service also failed due to corrosion. They should be of the diaphragm type with a non-freezing liquid.

7.4.5 Level Control

The stripper bottoms level control failed due to corrosion. The internal KEL-F coating was unsuitable for the 240 F acid sulfate solution. The float chambers on all level controls should be insulated, heat-traced, and have a provision for a bottom drain to avoid crystallization.

7.4.6 Forced Draft Fan

Fan vibrations and subsequent bearing failure was a continuous source of trouble. Most of these vibrations were a result of acid sludge buildup on the blades causing imbalance. Operation at fan inlet temperatures below 225 F increases deposition on the blades. This occurred only when the absorber overhead gas was recycled to control the SO2 inlet concentration. This should not be a factor in future work. Vibrations were reduced by water washing the fan blades. The fan blades were washed only when high vibration occurred causing flue gas flow interruption for only a few minutes.

7.4.7 Pumps

Sethco pump shaft failures were a major source of trouble. A different design should be used that avoids the hole in the shaft for the sleeve retainer. A condensate flush should be used for all packed pumps. Pumpage should not be used as seal flush since it does not remove salts from the packing material.

The Dorr-Oliver acid and caustic recycle pumps failed during the test program. Failure was traced to the radial seal which permitted attack of internal metal parts. Total operating time until failure was 30 days for the acid pump and about three months for the caustic pump. The construction of the Dorr-Oliver pumps is quite complex and repairs were difficult. Packing gland leakage from the acid recycle pump caused severe corrosion to the pump baseplate and pedestals.

7.4.8 Absorption Tower

No problems were experienced with the chemical section of the absorption tower. The plastic lining is intact as are all the internals. However, there was a problem in the quench section. A 316 stainless steel pad demister was installed between the impingement baffle tray and the lowest chimney tray. After several weeks of operation, the demister was completely corroded around the edges. Because the demister was installed during operation, the clearance between the pad and the chimney tray was only about one foot. This low clearance resulted in gas channeling which formed a stagnant ring around the edges of the demister as the flue gas passed through the restricted flow area. The acidic quench water (pH=2.5) in this ring attacked the demister and failure resulted. A polypropylene pad was installed and has operated satisfactorily for over six months.

7.4.9 Stripper Column

The packing support grid for the lower stage broke and dumped the packing into the reboiler. It is believed that pressure fluctuations, as a result of the rupture disc relieving on several occasions, contributed to the failure. The column performance was not diminished by the packing loss and operation continued using only one stage.

The carbon steel overhead reducer above the overhead condenser (T-101) corroded and failed after short service. A CPVC replacement performed quite well. However, CPVC has an upper temperature limit of 185 F and care was required to avoid overheating and ensure adequate condenser performance. The condenser tubes plugged periodically due to SO_2 hydrate formation. The blockage was cleared by raising the condenser outlet temperature.

The Kynar lined steel piping for the stripper bottoms flow failed on several occasions. These failures were attributabe to improper field "flaring" of the plastic liner allowing the process fluid to attack the carbon steel.

7.4.10 Cell Room

Cell room equipment operation was adequate at the operating levels reported in previous sections.

VIII

DISCUSSION OF ANALYTICAL PROBLEMS

8.1 BASIC ANALYSIS PROBLEMS

There were several analytical problems encountered during the test program. The following discussion details the problems associated with the major analyses encountered during operation and presents some general calibration data.

8.1.1 NaHSO3 / Na2SO3 / NaHCO3 / Na2CO3 / NaOH Analyses

The major analysis for the pilot plant was the determination of the absorption system net draw liquor composition. There are five possible species that can exist.

The quantitative determination of sodium bisulfite (NaHSO3) by titration with caustic was found to be quite acceptable for both pure and mixed bisulfite solutions. Titrations were carried out using a phenolphthalein end point, as well as a potentiometric end point. The potentiometric end point occurred at pH of 8.8, as determined by the titration of pure bisulfite solution. The results of the calibration runs in terms of the original solution normalties (1.0 N) and expressed as grams per liter are presented in Table 8.1. They do not reflect the final mixed concentrations of the species. Figure 8.1 presents the titration curve for sodium sulfite and sodium bisulfite as determined on site. The end points show excellent agreement with the published sulfurous acid equilibrium constants.

The quantitative determination of the sodium sulfite (Na2SO3) proved to be difficult. Direct titration with hydrochloric acid was found to yield results that were initially low. These results are also shown in Table 8.1. The acid titrations were carried out using both the methyl orange and potentiometric end point (pH 4.5). Furthermore, when a mixed sulfite-bisulfite solution was analyzed, the sulfite determination was even more inaccurate following the bisulfite titration with caustic soda.

The majority of the sulfite inaccuracy was found to be attributable to oxidation as a result of excessive exposure to the atmosphere. The evidence for this was:

a. No change in analysis occurred when boiled water was used for standard solution makeup (deoxygenated water).

b. 2.4 gm/l Na2SO4 was found in a titrated Na2SO3 solution (gravimetric analysis).

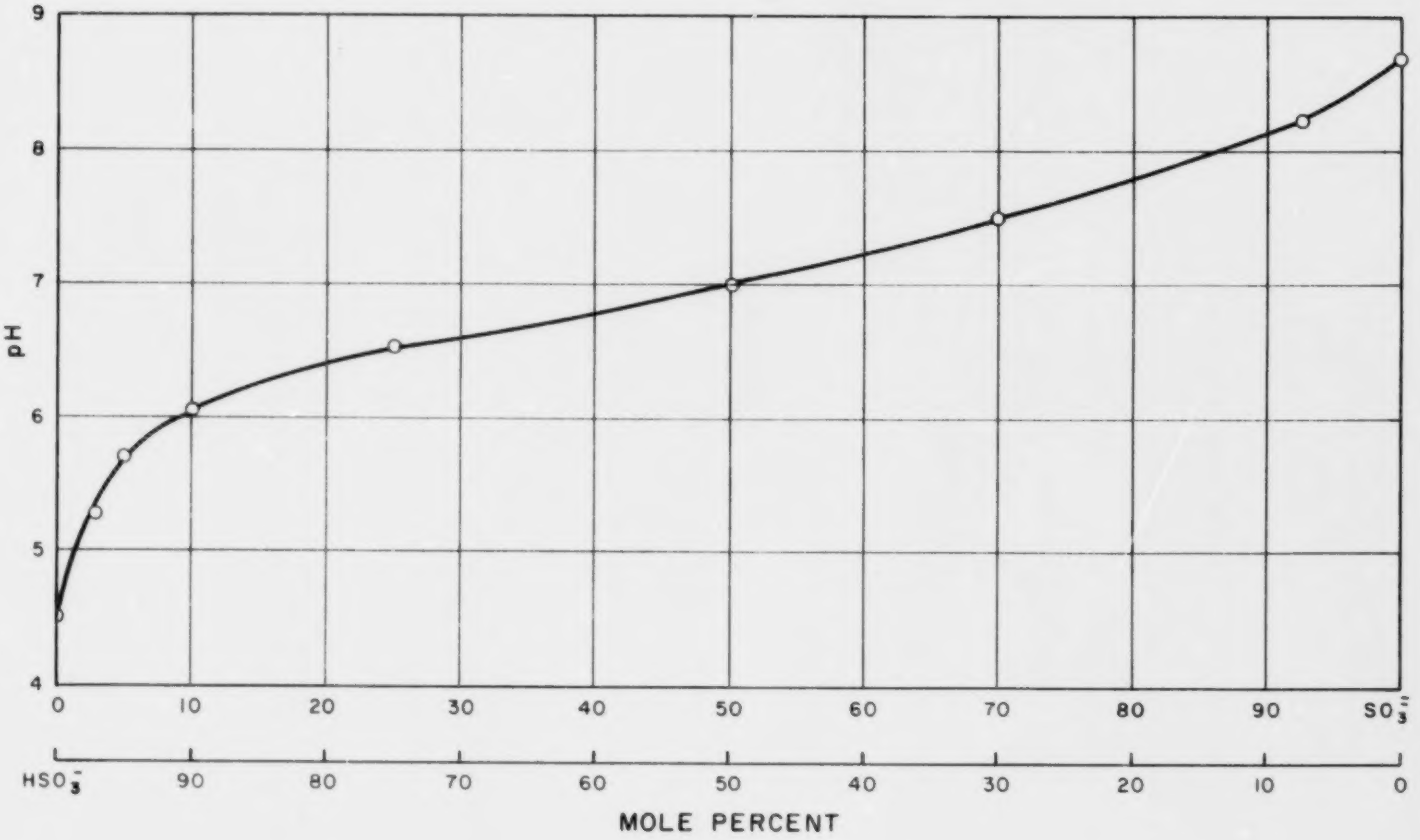

FIGURE 8.1 DISTRIBUTION OF AQUEOUS SULFITE SPECIES AS A FUNCTION OF pH

TABLE 8.1

SULFITE - BISULFITE DETERMINATION

SAMPLE		RESULTS (gm/l)		METHOD	NOTES
ml NaHSO3	ml Na2SO3	NaHSO3	Na2SO3		(Titration Method)
1		102.2		NaOH	Hand
1		106.9		NaOH	Machine
1		105.7		NaOH	Machine
1		105.7		NaOH	Machine
	1		115.4	HCl	Hand
	1		115.4	HCl	Machine
	1		119.0	HCl	Machine
	2		119.0	HCl	Machine
	2		111.8	HCl	Machine
2		105.5		NaOH	Machine
2		104.2		NaOH	Machine
2	1	104.5	100.0	NaOH/HCl	Machine
2	1	104.5	106.5	NaOH/HCl	Machine
	2		123.0	HCl	Machine
	2		120.0	HCl	using new solution
2		105.5		NaOH	Machine
2		104.2			
2	1	106.2	88.5	NaOH/HCl	Machine
	1		121.5	HCl	Machine
	1		118.0	HCl	Machine
2	1	95.8	112.0	HCl/NaOH	Machine
2	1	106.3	97.5	NaOH/HCl	#1 contrary to method
4	1	106.0	126.0	NaOH/Direct	Machine for NaOH
4	1	106.0	125.0	I2	Hand for I2

TABLE 8.1 - (CONT'D)

SULFITE - BISULFITE DETERMINATION

SAMPLE		RESULTS (gm/l)		METHOD	NOTES (Titration Method)
ml $NaHSO_3$	ml Na_2SO_3	$NaHSO_3$	Na_2SO_3		
4	1	105.0	116.0	NaOH/Excess	Machine for NaOH
4	1	106.0	116.0	I_2 then $Na_2S_2O_3$	Hand for $Na_2S_2O_3$
4	1	104.1	67.5	NaOH/HCl	Machine
4	1	106.0	45.4	NaOH/HCl	of above Solution
	0.5		111.9	excess I_2	Hand (new standard)
2	1	104.0	65.8	NaOH/HCl	Machine
2	1	104.0	65.8	NaOH/HCl	(with another new standard)
1	1	105.0	104.0	NaOH/I_2	Machine for NaOH
1	1	105.0	98.0	Direct	Hand for I_2
	1		125	I_2 Direct	Hand
	1		130	Excess I_2	
1	1	104.0	126.0	NaOH/I_2	Machine for NaOH
1	1	106.0	124.0	Direct	Hand for I_2
1	1	104.0	130.0	NaOH/Excess	Machine for NaOH
1	1	106.0	126.0	I_2 then $Na_2S_2O_3$	Hand for $Na_2S_2O_3$
	1		126.1	HCl	Hand
	1		125.0	HCl	(Immediately after
	1		126.1	HCl	Sample Prep)
1	1	104.0	126	NaOH/HCl	Hand for both
1	1	104.0	126	NaOH/HCl	(Immediately)
1	1	105.0	125	NaOH/HCl	

TABLE 8.1 - (CONT'D)

SULFITE - BISULFITE DETERMINATION

<table>
<tr><th colspan="2">SAMPLE</th><th colspan="2">RESULTS (gm/l)</th><th rowspan="2">METHOD</th><th rowspan="2">NOTES (Titration Method)</th></tr>
<tr><th>ml $NaHSO_3$</th><th>ml Na_2SO_3</th><th>$NaHSO_3$</th><th>Na_2SO_3</th></tr>
<tr><td>2</td><td>0.5</td><td>102.0</td><td>126</td><td>NaOH/HCl</td><td rowspan="2">Hand for both (Immediately)</td></tr>
<tr><td>2</td><td>0.5</td><td>103.0</td><td>126</td><td>NaOH/HCl</td></tr>
<tr><td colspan="6">The following series of samples were timed to note degradation. Bottles remained closed and titration was immediately after removing sample. All titrations were done by hand.</td></tr>
<tr><td>2</td><td>1</td><td>103</td><td>128</td><td>NaOH/HCl</td><td rowspan="2">0 hrs. time</td></tr>
<tr><td>2</td><td>1</td><td>103</td><td>128</td><td>NaOH/HCl</td></tr>
<tr><td>2</td><td>1</td><td>104</td><td>126</td><td rowspan="2">NaOH/Excess I_2 then $Na_2S_2O_3$</td><td rowspan="2">0 hrs. time</td></tr>
<tr><td>2</td><td>1</td><td>103</td><td>132</td></tr>
<tr><td>2</td><td>1</td><td>104</td><td>127</td><td>NaOH/HCl</td><td rowspan="2">3 hrs. time</td></tr>
<tr><td>2</td><td>1</td><td>104</td><td>126</td><td>NaOH/HCl</td></tr>
<tr><td>2</td><td>1</td><td>104</td><td>129</td><td rowspan="2">NaOH/Excess I_2 then $Na_2S_2O_3$</td><td rowspan="2">3 hrs. time</td></tr>
<tr><td>2</td><td>1</td><td>104</td><td>128</td></tr>
<tr><td>2</td><td>1</td><td>104</td><td>124</td><td>NaOH/HCl</td><td rowspan="2">20 hrs. time</td></tr>
<tr><td>2</td><td>1</td><td>104</td><td>125</td><td>NaOH/HCl</td></tr>
<tr><td>2</td><td>1</td><td>104</td><td>126</td><td rowspan="2">NaOH/Excess I_2 the $Na_2S_2O_3$</td><td rowspan="2">20 hrs. time</td></tr>
<tr><td>2</td><td>1</td><td>104</td><td>126</td></tr>
<tr><td>2</td><td>1</td><td>104</td><td>126</td><td>NaOH/HCl</td><td rowspan="2">0 hrs. time</td></tr>
<tr><td>2</td><td>1</td><td>104</td><td>126</td><td>NaOH/HCl</td></tr>
<tr><td>2</td><td>1</td><td>101</td><td>126</td><td>NaOH/HCl</td><td rowspan="2">3 hrs. time</td></tr>
<tr><td>2</td><td>1</td><td>101</td><td>124</td><td>NaOH/HCl</td></tr>
</table>

TABLE 8.1 - (CONT'D)

SULFITE - BISULFITE DETERMINATION

SAMPLE ml $NaHSO_3$	 ml Na_2SO_3	RESULTS (gm/l) $NaHSO_3$	 Na_2SO_3	METHOD	NOTES (Titration Method)
2	1	100.5	125	NaOH/HCl	6 hrs. time
2	1	100.0	126	NaOH/HCl	

The auto titrator was also used for the above series of samples. While the results are not reported, they were signifacantly low as in previous tests.

The following series of samples were used to test the effect of timed exposure to the air as well as the use of mannitol, an oxidation inhibitor.

(Samples titrated immediately)					
1	1	104	51.9	NaOH/HCl	Auto Titrator without Mannitol
1	1	100	82	NaOH/HCl	Auto Titrator with Mannitol
1	1	104.2	86	NaOH/HCl	
1	1	104.2	67.5	NaOH/HCl	Auto Titrator with Mannitol
(Samples exposed to air for two hours) (Mannitol added at start of exposure time)					
1	1	104.1	56.9	NaOH/HCl	Hand titration without Mannitol
1	1	103.5	121	NaOH/HCl	Hand titration with Mannitol
(Samples stirred and exposed to air for two hours. Mannitol added at start of exposure)					
1	1	104.0	0	NaOH/HCl	Auto Titrator without Mannitol
1	1	104.5	96	NaOH/HCl	Auto Titrator with Mannitol
(Samples stirred and exposed to air for two hours. Mannitol added at start of exposure.)					
1	1	104	2.5	NaOH/HCl	Hand titration without Mannitol
1	1	105	125	NaOH/HCl	Hand titration with Mannitol

TABLE 8.1 - (CONT'D)

SULFITE - BISULFITE DETERMINATION

SAMPLE		RESULTS (gm/l)		METHOD	NOTES (Titration Method)
ml $NaHSO_3$	ml Na_2SO_3	$NaHSO_3$	Na_2SO_3		
1	1	104	5	$NaOH/I_2$ Direct	Hand titration without Mannitol
1	1	104	124	$NaOH/I_2$ Direct	Hand titration with Mannitol
(Test of formaldehyde complexing method) (Samples titrated immediately)					
1	1	105	88	$NaOH/CH_3OH$-HCl	Auto titration
1	1	104	96	$NaOH/CH_3OH$-HCl HCl	Auto titration
1	1	104	118	$NaOH/CH_3OH$-	Hand titration
1	1	104	124	$NaOH/CH_3OH$-HCl	Hand titration

A sample of net draw liquor was also titrated as a function of time. Sample bottle was closed.

gm/L				
Na_2SO_3	Na_2CO_3	$NaHCO_3$	METHOD	NOTES
13.4	2.1	12.7	$NaOH/HCl/I_2$	0 hrs. time
13.4	2.1	12.7	$NaOH/HCl/I_2$	3 hrs. time
13.3	2.1	12.7	$NaOH/HCl/I_2$	

NOTE: (1) Both sulfite and bisulfite solutions used were 1.0 N solutions.
(2) All results adjusted to reflect input normality.

c. Continued sample degradation upon exposure to atmosphere.

d. Accuracy increased upon the addition of an antioxidatant (mannitol).

The initial solutions were titrated using an automatic titrator which, for a particular sample requiring both caustic and acid titration, meant that the sample was exposed to the atmosphere for at least ten to fifteen minutes. These titrations yielded quite low results. However, upon reverting to hand titrations and minimizing exposure time, the test accuracy was increased.

The fact that sodium sulfite is the oxidized species, is confirmed in Section 6.2. The accuracy of the acid titrations directly reflects the overall analytical accuracy in that carbonates and bicarbonates are determined by difference. The iodometric determination of total dissolved SO_2, either by direct titration with iodine or by the back titration of excess iodine with sodium thiosulfate ($Na_2S_2O_3$) also proved to be satisfactory when done rapidly. The iodine titration follows the equation:

$$Na_2SO_3 + I_2 + H_2O \longrightarrow Na_2SO_4 + 2HI \qquad (1)$$

(with excess I_2)

$$Na_2SO_3 + I_2 + H_2O \longrightarrow Na_2SO_4 + 2HI + I_2 \qquad (2)$$

and the back titration with $Na_2S_2O_3$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI \qquad (3)$$

The pH of the solution for equations (1) and (2) should be less than 8.0 to prevent the formation of hypoidous acid

$$I_3 + OH \longrightarrow HIO + 2I \qquad (4)$$

which in turn, oxidizes S_2O_3 to SO_4 instead of tetrathionate as given in equation (3).

The acid/base titration was used for sulfite-bisulfite determination. Iodine titration was used to determine the total SO_2 in solution and the difference between the two titrations used as a measure of carbonates, if there were carbonates present. The test accuracy was approximately one percent for the sulfite-bisulfite determination.

During the course of the calibration work on this system, another method was tried for sulfite-bisulfite determination. Formaldehyde addition complexes the sulfite ion with the stoichiometric release of NaOH. Therefore, in a sulfite-bisulfite titration, one would titrate with caustic to the phenolphthalein end point, thereby converting all bisulfite to sulfite, add formaldehyde, and titrate with acid to the phenolphthalein end point again. This method has the advantage of very sharp potentiometric end points, but the use of formaldehyde in a confined field laboratory without a hood precluded its use. This method did, however, yield results comparable to the other methods, the difference being in the sulfite concentration.

In order to limit sample oxidation during storage and analysis, mannitol was added to each sample. Mannitol is a carbohydrate ($C_6H_{14}O_6$) anti-oxidant. Its use proved quite successful in limiting sample oxidation as can be seen in Table 8.1 by comparing the timed titration both with and without mannitol addition. While one closed sample showed only slight degradation over a 24 hour period, mannitol was, nevertheless, added to each sample in order to prolong sample shelf life.

During the later part of the test program, as the total SO_2 solution increased due to increased system loading, sodium bicarbonate appeared more frequently and at significantly higher concentrations. Several samples of solutions containing high bicarbonate levels were analyzed for total carbon at a commercial laboratory in order to determine if the bicarbonate levels were real or a result of titration errors. Table 8.2 presents the laboratory-determined results. Obviously, the titrations were in error. In these determinations, the iodine titration was used for total sulfur as SO_2 and compared to that obtained from the acid titration which includes the amount of bicarbonate present. Thus, either the iodine titration was low or the acid titration was high. It is believed that with more controlled laboratory conditions, the overall test accuracy can be increased.

8.1.2 Na_2SO_4

The analytical determination of sodium sulfate is extremely important with respect to oxidation calculations. The sulfate formation due to oxidation is usually a small percentage of the total sulfate in solution. For example, if 100 liters/hr of caustic solution containing 200 gm/l of sodium sulfate were fed to the absorption tower to effect the removal of 1.0 g-mole/hr of SO_2, absorber oxidation in the amount of ten percent would add only 6.4 grams/liter to the sulfate already in the caustic. This is equivalent to a 3.2 percent increase in the total sulfate concentration.

TABLE 8.2

BICARBONATE IN ABSORBER LIQUID

Sample Number	HCO3 - Determined On Site - Titration Difference (Grams/Liter)	HCO3 - Determined by Skinner & Sherman with a Total Carbon Analyzer (ppm)
1358	2.6	546
1368	3.11	714
1375	7.31	426
1379	3.44	546
1387	6.97	1010
1422	4.12	524
1449	3.61	814
1461	3.78	716
1533	10.25	626
1534	5.12	774
1537	10.92	906
1545	12.60	708

The solution sulfate concentrations were determined gravimetrically by precipitation with barium chloride. This methodology has been used for sulfur determination for many years. However, it is prone to errors, especially errors of coprecipitation and occlusion. Furthermore, all sulfite and bisulfites must be removed by acidification and stripping prior to the barium chloride addition in order to avoid precipitation of barium sulfite. Table 8.3 summarizes the calibration samples and their analysis.

They exhibit an overall standard deviation of five percent, which is well above that required for a definitive oxidation calculation. This error was the major reason for the large amount of data scatter experienced. An alternate method for sulfate determination should be considered such that the overall accuracy is less than one percent of the total sulfate present.

8.2 IRON ANALYSIS

In the analytical scheme setup for the WEPCO SO2 removal pilot plant, iron determinations from the various plant streams were assigned to a Milwaukee-based commercial laboratory, Limnetics, Inc.

Of the samples withdrawn for Fe analyses, cell feed liquor samples were of primary importance. Iron levels exceeding 0.1 ppm in the cell feed liquor were considered to be detrimental to the cell operation. Analytical results obtained from Limnetics, however, showed a systematic tenfold increase over the permissible safe iron levels; yet, no serious deterioration in the cell performance was experienced. Reconciliation of the obviously conflicting facts can only be explained (a) by a much higher than anticipated tolerance of the cells for iron or (b) by erroneous iron analyses. In checking the latter possibility, comparison of Fe determinations were simultaneously made on standard and test solutions in both Limnetics and Ionics laboratories. The iron determinations were run in approximately 3 N aqueous sodium sulfate solutions containing about 213 g Na_2SO_4 per liter.

Limnetics used the instrumental atomic absorption (AA) analytical technique by direct aspiration. Ionics applied the phenanthroline colorimetric method for the iron determination.

In Table 8.4, a summary of the results received from the two sources is shown. Along with these data, results of a later comparison study at the Institute of Gas Technology (IGT), Chicago, were also entered.

TABLE 8.3

SODIUM SULFATE ANALYSIS GRAVIMETRIC DETERMINATION

Sample	STANDARD Na2SO4 (gm/l)	NaHSO3 (gm/l)	Na2SO3 (gm/l)	RESULTS Na2SO4 (gm/l)	PERCENT ERROR
258	150	-	-	145/138	-3.3/-8.0
259	200	-	-	196/188/189	-2.0/-6.0/-5.5
A	200	-	-	207	+3.5
B	150	-	-	152	+1.3
C	200	80	-	205	+2.5
D	150	80	-	154	+2.7
E	200	80	20	191	-4.5
F	150	80	20	162	+8.0
590	150	50	20	165	+10.0
620	142	-	-	154	+8.5
621	213	-	-	224	+5.2
622	284	-	-	282	-0.7
623	213	52	-	221	+3.8
624	213	104	-	215	+0.9
625	213	130	-	229	+7.5
1079	100	-	-	96	-4.0
1080	100	105	-	103	+0.3
1129	150	100	-	157	+4.7
1171	150	100	-	157	+4.7
1253	150	100	-	143	-4.7
1254	143	100	(+2N NaOH)	148	+3.9
1446	150	100		151/152	+1.0
1532	150	100		162	+8.0

Average = +1.3

Standard Deviation = +5.1

TABLE 8.4

IRON ANALYSES IN 3 N SODIUM SULFATE SOLUTIONS

Source (Sample No.)	Stream	Limnetics	Ionics		IGT
		ppm Atomic Absorption (Direct Aspiration)	ppm Phenanthroline (Colorimetric)	AA (Extraction)	(g/ml Ferrozine Colormetric)
584	Upstream Mn Zeolite	0.8	0.11	0.04	0.54
585	Downstream Mn Zeolite	0.8	0.02	0.01	0.58
586	Upstream Mn Zeolite	0.9	0.14	0.10	0.64
587	Downstream Mn Zeolite	0.9	0.02	0.01	0.74
588	Stripper Bottoms	42.0	1.8	35	46
589	Cell Feed	1.3	1.5	1.4	1.9
Standard Samples					
1 (3 ppm Fe)		11.4	3.8	3.3	3.9
3A (0.5 ppm Fe)		7.5	0.8	0.48	1.0

Comparing the two sets of data in columns 1 and 2, the generally much higher trend in the Limnetics results was obvious. The prepared standard samples seemed to indicate, after allowing for the amount of iron introduced as Na2SO4 impurity, that the results furnished by Limnetics were in serious error.

The analytical laboratory of the Institute of Gas Technology (IGT) investigated the effect of the presence of a large quantity of sodium sulfate on the iron determinations. The same test and standard solutions, as used earlier by the other two sources, were submitted for the analysis.

IGT conducted a systematic study using both AA and colorimetric approaches. A technical report (Appendix G) was prepared detailing the results of the investigation from which the following primary conclusions were made:

1. Direct aspiration of a concentrated (3 N) sodium sulfate solution into the AA unit for iron determination is unworkable and was responsible for the erratic Limnetics results.

2. Reducing the salt concentration by water dilution renders the direct aspiration AA workable; however, in case of low iron concentration, dilution can depress the Fe level beyond its detectability.

3. Removing the iron from the aqueous electrolyte medium into an organic phase by extraction and using the extract for the determination is the most promising and safest method for specific Fe determination with AA.

8.3 OTHER ANALYSES

Some comments are in order on several other analytical problems encountered during the test program.

The determination of the total sodium in the plant streams should be done by atomic absorption. A sodium specific electrode gave very erratic results due to the high dielectric constant of the solutions; specific ion electrode determinations are most applicable for dilute salt solutions. Table 8.5 compares total sodium as analyzed by atomic absorption versus total sodium in certain standard samples.

Dilute SO2 gas samples are quite sensitive to degradation with time if taken in glass burettes for subsequent gas chromatographic analysis. Samples determined online by the Intertech at several thousand ppm SO2 degraded completely within 24 hours in glass burettes. This was not true of the concentrated SO2 samples taken in the stripper overhead. Absorber interstage gas samples should be analyzed immediately, preferrably using the Intertech analyzer or a similar online device.

TABLE 8.5

TOTAL SODIUM ANALYSIS

SAMPLE	STANDARD Na (mg/l)	ATOMIC ABSORPTION RESULTS (mg/l)	PERCENT ERROR
A	94,200	93,600	-0.6
B	37,700	34,000	-9.8
C	18,800	19,000	+1.1

IX

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X

APPENDICES

A. LIMNETICS, INC. REPORT ON FOREIGN MATERIAL ANALYSIS AS SUBMITTED BY IONICS, INCORPORATED

B. WEPCO PILOT PLANT OPERATING LOG

C. OXIDATION CALCULATIONS

D. SULFUR REMOVAL CALCULATIONS

E. BRITISH TO METRIC CONVERSION TABLE

F. TABULAR SUMMARIES AND MEASUREMENTS

G. IGT TRACE IRON ANALYSIS

APPENDIX A
LIMNETICS, INC., REPORT ON FOREIGN MATERIALS ANALYSIS*

Concentrations of various foreign materials in the process streams were determined from time to time during the pilot program. An example of such an analysis, made by Limnetics, Inc., early in the pilot program, is given in Table A-1. Such analyses are frequently very useful for diagnostic purposes. The interpretation of the data in the table is as follows:

1. Sodium: This element is conveniently used as a tracer. The Cell Feed (Column E – 51,000 ppm) is sent as feed to the Combined Catholytes (Column D) and the center compartments. Sodium ion is transferred through the cathode cation exchange membranes into the catholyte so one expects the Combined Catholytes (Column D – 90,000 ppm) to have a substantially higher concentration of sodium. This is indeed the case. One also expects the "A" Anolyte Effluent (Column A - 45,000 ppm) and the "B" Mid-Anolyte Effluent (Column C - 43,800 ppm) to have reduced concentrations of sodium owing to transfer of sodium into the catholytes. The apparent reduction in concentration is low, however, owing to the expected electroendosmotic water transfer accompanying sodium ions from the center compartment to the catholytes. The "B" Mid-Anolyte (Column C) is separated from the "B" Anolyte (Column B - 15.0 ppm) by an anion exchange membrane which permits substantially only transfer of sulfate ions from the "B" Mid-Anolyte to the "B" Anolyte and of hydrogen ions from the "B" Anolyte to the "B" Mid-Anolyte. The low concentration of sodium in the "B" Anolyte (Column B - 15.0 ppm) is typical and completely expected.

The Combined Catholytes (Column D – 90,000 ppm) are fed to the Absorber (Column F). The Drawdown from the latter (65,000 ppm) is much less than 90,000 ppm and indicates a substantial liquid carry-over from the Quench section of the Absorber. This conclusion was confirmed by other results indicated below. Subsequent measurements on the Absorber confirmed such a substantial carry-over from the Quench section.

2. Potassium: This element is also conveniently used as a tracer. The concentrations in the system are at least an order of magnitude less than those which might cause any problems. At such much higher concentrations, the first effect would probably be the crystallization of potassium pyrosulfite. The concentrations of potassium ion in the

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(*) As submitted by Ionics, Inc., Watertown, MA 02172.

TABLE A-1

LIMNETICS, INC., ANALYSES OF VARIOUS WEPCO PROCESS STREAMS SAMPLED AUGUST 22, 1973
(PARTS PER MILLION)

Item	A "A" Anolyte Effluent	B "B" Anolyte Effluent	C "B" Mid-Anolyte Effluent	D Combined Catholytes	E Cell Feed	F Absorber Drawdown	G Stripper Bottoms	H Quench Return
1. Sodium	45,000	15.0	43,800	90,000	51,000	65,000	50,000	30
2. Potassium	145	0.6	130	400	170	250	175	4.0
3. Calcium	5.2	0.05	5.6	1.3	5.6	5.3	6.3	52.0
4. Magnesium	2	<1	<1	<1	2	10	5	38
5. Aluminum	<0.5	<0.5	<0.5	<0.5	<0.5	0.6	0.5	<0.5
6. Manganese	0.30	0.06	0.36	0.23	1.35	0.35	0.60	0.15
7. Iron*	1.8	2.0	1.4	1.8	1.6	3.6	58.0	3.6
8. Chromium	0.21	<0.02	0.10	0.15	0.12	0.63	0.43	1.0
9. Nickel	1.9	0.4	1.6	2.2	1.8	2.4	2.1	0.3
10. Lead	5.6	3.8	1.5	1.7	1.4	2.0	3.5	<0.02
11. Zinc	0.63	0.28	0.56	0.54	0.58	0.68	0.62	<0.02
12. Nitrates (as N)	130	110	18	30	29	<0.01	13	0.8
13. Nitrites (as N)	0.004	0.004	0.004	<0.002	<0.002	<0.002	0.006	0.012
14. Chloride	152	38	698	161.5	741	29,000	950	152

*These iron analyses by Limnetics, Inc., found to be incorrect, see Section 8.2.

various process streams follow those of sodium and confirm the probability of substantial carry-over of liquid from the Quench section into the absorber.

3. Calcium: The highest value of calcium in the various process streams is found in the Quench Return (Column H - 52.0 ppm). The latter is the probable source of calcium in the system through liquid carry-over into the Absorber section. The difference between the value in the Cell Feed (Column E - 5.6 ppm) and the Combined Catholyte (Column D - 1.3 ppm) indicates that one should expect precipitation of calcium compounds in the mid-catholyte and center compartments. The precipitates found in these compartments did contain a high concentration of calcium.

The low concentration of calcium in the "B" Anolyte Effluent is as expected from the use of anion exchange membranes separating the "B" Anolyte from the "B" Mid-Anolytes.

The difference in concentration between the Combined Catholytes (Column D - 1.3 ppm, which is feed to the Absorber) and the Absorber Drawdown (Column F - 5.3 ppm) again confirms the carry-over of Quench Return into the Absorber.

4. Magnesium: The analyses for this ion again illustrates the carry-over of Quench Return (Column H - 38 ppm) into the Absorber Drawdown (Column F - 10 ppm). The Combined Catholyte (Column D) fed to the Absorber contained only <1.0 ppm. The difference between the Cell Feed (Column E - 2 ppm) and the Combined Catholytes (Column D - <1 ppm) again predicts magnesium precipitate in the center and Mid-catholyte compartments. Such magnesium bearing precipitates were found in these compartments. The difference in concentration between the Cell Feed (Column E - 2 ppm) and the Stripper Bottoms (Column G - 5 ppm) probably indicates the precipitation of magnesium hydroxide at alkaline pH's in the main cell feed storage tanks. The difference in concentration of this ion between Stripper Bottoms (Column G - 5 ppm) and Absorber Drawdown (Column F - 10 ppm) is caused by adding "A" Anolyte Effluent (Column A - 2 ppm) and "B" Mid-Anolyte Effluent (Column C - <1 ppm) to the Absorber Drawdown to strip off sulfur dioxide in the Stripper.

5. Aluminum: The aluminum levels are essentially undifferentiated by the sensitivity of the analysis. It was concluded, however, that the dissolution of aluminum hydroxide from the manganese zeolite filter by high pH cell feed experienced earlier in the pilot program had been corrected. The aluminum levels are acceptable.

6. Manganese: This ion catalyzes the oxidation of sulfite by oxygen in the Absorber and should be kept at low

levels. The highest concentration of manganese is found in the Cell Feed (Column E - 1.35 ppm) indicating pick-up from the manganese zeolite filter presumably from excessive sulfite in the Cell Feed. The difference between the Cell Feed (Column E - 1.35 ppm) and the Combined Catholytes (Column D - 0.23 ppm), the "A" Anolyte Effluent (Column A - 0.30 ppm) and "B" Mid-Anolyte Effluent (Column C - 0.36 ppm) indicates precipitation of manganese compounds in the mid-catholyte and center compartment cells. Indeed, moderate amounts of manganese were found in the precipitates in these compartments, probably present as the carbonate.

7. Iron (see note): This ion also catalyzes the oxidation of sulfite by oxygen in the Absorber and should be kept at low levels. The highest concentration of iron is found in the Stripper Bottoms (Column G - 58.0 ppm) indicating corrosion of some component. (It was later found that a steel spool piece in the top of the Stripper and an inadvertently unlined length of steel pipe carrying bottoms from the stripper had been corroding. Both were replaced with plastic lined components.) The difference between the Stripper Bottoms (Column G - 58.0 ppm) and the Cell Feed (Column E - 1.6 ppm) indicates that the various filters between the Stripper and the Cell are indeed removing iron but not quite well enough. The undesirably high levels in the Cell Feed are probably due to the sulfite loading contributed by the Stripper. The comparatively high level of iron in the Absorber Drawdown (Column F - 3.6 ppm) indicates corrosion of some component in the Absorber (such as the stainless steel rods on which corrosion test coupons were mounted or perhaps the coupons themselves) or carry-over from the Quench Return.

Note: Analyses for iron in concentrated Na_2SO_4 (3N) by Limnetics, Inc. were later found to be in error. Nevertheless, the relative amounts of iron in the various streams are correct.

The high level in the "B" Anolyte Effluent is unexpected and either indicates corrosion of some component in the "B" Anolyte circuit or contamination in the water fed to the "B" Anolyte.*

8. Chromium: The highest level is found in the Quench Return (Column H - 10. ppm), liquid carry-over of which into the Absorber is probably responsible for much of the high value in the Absorber Drawdown (Column F - 0.63 ppm), the remainder coming from the Combined Catholyte (Column D - 0.15 ppm) and from corrosion of chromium containing coupons and support rods in the Absorber. The concentration in the

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*It was later found that the latter was the principal case. The water was subsequently treated to remove the iron by ion-exchange demineralizers.

Stripper Bottoms (Column G - 0.43 ppm) is adequately explained by dilution of the Absorber Drawdown with "A" Anolyte Effluent (Column A - 0.21 ppm) and "B" Mid-Anolyte Effluent (Column C - 0.10 ppm). The difference in concentration between the Stripper Bottoms (Column G - 0.43 ppm) and the Cell Feed (Column E - 0.12 ppm) indicates a removal process, presumably precipitation and filtration of the gray-green gelatinous, hydrous chromium sesquioxide. The level in the "B" Anolyte Effluent is satisfactory and probably indicates that the iron alloy (such as Hastelloy C) corroding in the "B" Anolyte circuit contains only a low amount of chromium. The level in the "A" Anolyte Effluent (Column A - 0.21 ppm) is significantly higher than the Cell Feed (Column E - 0.12 ppm) and probably indicates corrosion of a stainless steel type alloy in the "A" Anolyte circuit.

9. Nickel: This ion also catalyzes the oxidation of sulfite by oxygen in the Absorber and should be kept at low levels. The highest level is found in the Absorber Drawdown (Column F - 2.4 ppm) and indicates corrosion of some stainless steel components, presumably the stainless steel rods used to support the corrosion test coupons in the Absorber. The concentration in the Stripper Bottoms (Column G - 2.1 ppm) is adequately explained by dilution of the Absorber Drawdown with "A" Anolyte Effluent (Column A - 1.9 ppm) and "B" Mid-Anolyte Effluent (Column C - 1.6 ppm). The small difference between the Stripper Bottoms (Column G - 2.1 ppm) and the Cell Feed (Column E - 1.8 ppm) indicates that the Cell Feed conditioning system is not very effective in removing this contaminant. The somewhat higher concentration in the Combined Catholyte (Column D - 2.2 ppm) compared to the Cell Feed indicates that much of the nickel is soluble and is being transferred through the cathode cation exchange membrane. The high value in the "B" Anolyte Effluent (Column B - 0.4 ppm) indicates corrosion of an iron-nickel alloy (such as Hastelloy C) containing a low level of chromium in the "B" Anolyte circuit (see paragraphs 7 and 8 above). The levels of nickel in the various cell effluents compared with the Cell Feed indicate that we should not find significant quantities of nickel in any precipitates in the cells. This was found to be the case.

10. Lead: The highest levels of lead are found in the "A" Anolyte Effluent (Column A - 5.6 ppm) and "B" Anolyte Effluent (Column B - 3.8 ppm). These levels are both higher than expected probably due to the high chloride levels (line 14, columns A and B) in the two effluents (see paragraph 14 below). Both the lead and chloride levels in the "A" Anolyte Effluent are higher than in the "B" Anolyte Effluent. The concentration of lead in thee Absorber Drawdown (Column F - 2.0 ppm) compared with the Combined Catholytes (Column D - 1.7 ppm) is surprisingly high considering the dilution of Absorber Drawdown by Quench Return indicated by other evidence. The most probable

explanation of this value is that the system is not at steady-state with respect to chloride. Note that the Stripper Bottoms (Column G, line 14) contain about 950 ppm chloride compared to 152, 698, 162, and 741 in the "A" Anolyte Effluent, "B" Mid-Anolyte Effluent, Combined Catholytes, and Cell Feed, respectively. The lead level in the Absorber Drawdown corresponds to that in a volume of Combined Catholyte made several hours before. As will be shown in Paragraph 14 below, the system rejects chloride and hence, both the lead and chloride levels should decrease with time.

The higher than expected levels of lead in the "A" and "B" Anolyte Effluents indicate higher than expected, but not catastrophic, attack on the lead anodes. As will be discussed in Paragraph 14, the chloride levels in the process streams should be reduced.

The difference in levels between the Stripper Bottoms (Column G - 3.5 ppm) and the Cell Feed (Column E - 1.4 ppm) indicates substantial removal of lead by the Cell Feed conditioning subsystem.

11. Zinc: This ion is not expected to cause any difficulties at the concentrations found in the various process streams. However, the very low level found in the Quench Return compared with the other process streams indicates dissolution of some zinc containing component in the latter process streams. The value found in the "B" Anolyte Effluent (Column B - 0.28 ppm) is particularly surprising. Possible sources are zinc compounds (zinc oxide, zinc stearate) used in the molded rubber cell components; as mold release agents for such components; as heat and light stabilizers in CPVC or PVC components; as mold release or extrusion lubricants for such components. Less likely but also possible are Babbit metal, solder, or a brass or bronze component in the circuit.

12. Nitrates: The high levels of nitrate in the "A" and "B" Anolyte Effluents (Columns A and B - 130 and 110 ppm, respectively) indicate probably corrosion of the nitrile rubber anode frames by oxidants in the anolytes. It is suspected that the corrosion rate is aggravated by the high level of chloride in the process stream. At the anodes, such chloride should be oxidized to chlorine which is known to attack nitrile rubber. The anode frames in the commercial scale plant will be filled polypropylene, known to resist wet chlorine attack.

The low level of nitrate in the Absorber Drawdown (Column F - <0.01 ppm) is surprising compared to the 30 ppm in the Combined Catholytes (Column D), the feed to the Absorber. The low level may indicate catalytic reduction of nitrate by bisulfite under acid conditions through the transition element ions (Mn, Fe, and Ni) as intermediaries.

One would also expect attack of ferrous alloys (such as the stainless steel support rods for the corrosion test coupons in the Absorber) by dilute nitrate under acid conditions. The reported low level may also mean some interference by the high levels of bisulfite or sulfite with the nitrate analysis used.

The difference between nitrate in the Stripper Bottoms (Column G - 13 ppm) and in the Cell Feed (Column E - 29 ppm) is unexplainable. The difference between Cell Feed and "B" Mid-Anolyte Effluent (Column C - 18 ppm) may be explained as transfer of nitrate from the Mid-Anolyte compartment through the anode anion exchange membrane into the "B" Anolyte.

13. Nitrite: The nitrite levels in all streams are unremarkable and at very low levels.

14. Chloride: Chloride levels in all process streams (other than the Quench Return) are very high and generally unsatisfactory. The 29,000 ppm reported for the Absorber Drawdown appears to be in error and is otherwise unexplainable. Comparing the level in the Stripper Bottoms (Column G - 950 ppm) with that in the Quench Return (Column H - 152 ppm) indicates that the high levels in the system did not come from the Quench Return. It was later found that the chloride was a contaminant in the initial charge of diaphragm caustic soda into the system. Chloride is a substantial contaminant of diaphragm grade caustic. Low chloride, rayon grade caustic should be used as charge and makeup. The differences between Cell Feed (Column E - 741 ppm) and the Stripper Bottoms (Column G - 950 ppm) and between the Cell Feed and the Combined Catholytes (Column D - 162 ppm) cannot be satisfactorily explained. The Stripper Bottoms levels (Column G - 950 ppm) would be expected to be a weighted average of Combined Catholytes (Column D - 162 ppm), "A" Anolyte Effluent (Column A - 152 ppm), and "B" Mid-Anoltye Effluent (Column C - 698 ppm) but clearly is not. The differences may perhaps be explained by differences in the time at which the samples were collected since the system is rejecting chloride, probably as gaseous chlorine in the oxygen gas produced at the "A" and "B" Anodes. For example, the concentration in the "A" Anolyte Effluent is 152 ppm (Column A) compared to 741 ppm in the Cell Feed (Column E) to that anode. One would expect chloride to be transferred across the "B" cell anode anion exchange membrane from the "B" Mid-Anolyte compartment (Column C - 698 ppm) into the "B" Anolyte compartment (Column B - 38 ppm) and part of that chloride converted to gaseous chlorine.

APPENDIX B
CHRONOLOGICAL HISTORY OF PILOT PLANT OPERATIONS*
JUNE 1, 1973 - MAY 9, 1974

June 1-June 19, 1973

Debugging and preliminary operation with flue gas and process fluids.

June 19-June 29, 1973

Vendor repaired tank, J-104, which had failed.

June 29-July 6, 1973

Prepared new feed liquor charge and processed through the cells.

July 6, 1973

WEPCO accepted plant and integrated plant operation was started.

July 7, 1973

Shutdown after 24 hours due to low levels in caustic and feed liquor tank and plugging of cell system. Reason for low levels was excessive pump packing leakage, absorber carryover, and cell venting. Plugging of cells was due to metals released from water conditioner.

July 7-July 10, 1973

Diagnosed problems and flushed cell system.

July 10, 1973

Restarted cells.

July 11, 1973

Restarted integrated plant operation. Shutdown after six hours because of plugging in cells.

July 11-August 3, 1973

Obtained analysis of various streams and contaminants in order to diagnose problem. Identified problem and took corrective action which included relocating the water conditioner, and the installation of a new automatic pH control system.

(*) WEPCo Pilot Plant, S & W/Ionics Process, Milwaukee, Wisconsin.

August 3-August 5, 1973

Preliminary operation and debugging of new pH control system. Cells restarted to process feed liquor.

August 5, 1973

Restarted integrated plant operations.

Shut down plant after five hours due to excessive vibration of fan R-101.

August 5-August 7, 1973

WEPCo balanced fan and a new batch of feed liquor was prepared.

August 7, 1973

Restarted integrated plant operation.

Shut down plant after 13 hours operation due to low level in caustic tank.

August 7-August 9, 1973

Built up level in caustic tank with only the "A" cells able to operate, since "B" cell rectifier had failed.

August 9, 1973

Restarted integrated plant operation.

Shut down after five hours operation due to excessive vibration of fan R-101.

August 9-August 13, 1973

WEPCo rebalanced the fan and Ionics repaired the "B" cell rectifier circuit.

August 13, 1973

Restarted integrated plant operation.

August 16, 1973

Shut down after 68-hour run due to packing failure of P-102A.

August 16-August 19, 1973

WEPCo repacked P-102A ten times.

August 19, 1973

Restarted cells.

August 20, 1973

Restarted integrated plant operation.

August 21, 1973

Shut down after 26 hours due to failure of weld in stripper overhead spool piece. Cells continued to run.

WEPCo repaired spool piece.

Restarted integrated plant operation.

August 24, 1973

Shut down after 69 hours due to low level in caustic tank which was caused by gradual fall-off of cell performance.

August 24-October 3, 1973

Cells were disassembled and some parts were returned to Watertown for evaluation. Analyses were made of all major streams to determine source of contaminants. Various modifications requiring new materials were made to the plant to avoid future problems. New cell components were manufactured and installed. Calibration of instruments and entrainment tests were conducted during the shutdown. Existing liquor inventories were dumped, tanks washed and a new batch of feed liquor was prepared.

October 3, 1973

Restarted integrated plant operation. Frontend: 1650, Cells: 2100

October 6, 1973

Shut down after three-day run due to failure of P-105 motor overload relay (1650).

October 6-October 9, 1973

WEPCo obtained a replacement relay for P-105, and cleaned fan R-101.

October 9, 1973

Restarted integrated plant operation (1410).

October 11, 1973

Shut down due to excessive vibration of fan R-101, caused by fly ash deposition in fan (0830).

October 11-October 15, 1973

WEPCo cleaned and balanced the fan. Also, it was necessary to align the suction piping flange and repair the foundation grout which had failed due to past vibration of the fan.

October 15, 1973

Restarted integrated plant operation.

October 16, 1973

Shut down after 24-hour run due to failure of the WEPCO #4 boiler discharge main steam line.

October 16-October 26, 1973

During the shut down, the absorber quench section demister was found to be severely corroded. A replacement polypropylene demister was ordered and installed. An air purge was added upstream of the stripper overhead pressure control to improve pressure control. The hydrogen peroxide injection system was readied. A broken pump shaft (P-102A) was replaced.

October 26, 1973

Restarted integrated plant operation.

November 6, 1973

Shut down after 11-day run. The cause was corroded spool piece on stripper overhead and corroded FIC-15.

November 6-November 13, 1973

Replaced spool piece with CPVC piece, repiped stripper feed line to reduce carryover to condenser which had been subject to plugging, reversed cooling water flow to condenser, repaired FIC-15 and filled with buffer fluid, replaced LC-34 with a spare absorber LC, repaired solenoid in cell area.

November 13, 1973

Restarted integrated plant operation.

November 17, 1973

Shut down due to high DP in cells, and fan bearing failure.

November 17-November 24, 1973

Replaced bearing, backwashed cells; also repaired FIC-15 and LC-34 and recharged water conditioner with new "green sand".

November 24, 1973

Restarted integrated plant operation.

Shut down due to broken shaft on absorber circulation pump.

November 24-December 5, 1973

Replaced shaft. Removed acid pump for repair in WEPCo shop because pump had corroded between baseplate and pump.

December 5, 1973

Restarted integrated plant operation (0800).

December 6, 1973

Shut down due to power failure caused by short in mixer motor (0230).

December 6-December 16, 1973

Noticed leaking mechanical seals in cell area pumps and leaking shaft seal in acid pump. Ordered and replaced parts in pumps. Christmas rush delayed air shipment of pump parts and when arrived one part ordered was missing. Missing part was hand carried to site by Vendor. Also, impeller was stock size and had to be turned down in WEPCo shop.

December 16, 1973

Restarted integrated plant operation (1400/1000).

December 20, 1973

Shut down due to ground fault in cable to fan motor.

December 20-December 23, 1973

Repaired fault. Also noticed mysterious white gummy material in lower circuit of absorber which had to be washed out of circuit. Sent sample to downtown lab for analysis.

December 23, 1973

Restarted integrated plant operation.

December 25, 1973-January 2, 1974

Shut down due to leaks from the lined pipe between the stripper and T-103. Located replacement materials; fabricated and reinstalled pipe by December 28. Drips from pipe caused a small electrical fire which destroyed a switch box which controls lab power and electrical tracing circuits. WEPCo completed electrical repairs associated with the fire on December 31. During startup on January 1, the WEPCo turbine serving No. 3 and No. 4 boilers tripped, and the pilot plant was returned to shut-down status pending stable operation of the WEPCo power house which was achieved the evening of January 1, 1974.

January 2, 1974

Cold weather caused a slow startup, but integrated plant operation resumed late on January 2.

January 8, 1974

Shutdown at 1600 hours due to cracking stripper bottoms drum outlet nozzle. Crack caused by incorrect installation of pipe hanger and clamp.

January 11, 1974

Plant restarted at 1100 hours. Cell startup delayed by crystallization in the cell components.

January 12

Cell system started at 1100 hrs. Front end shutdown at 1200 hrs due to fan vibration. All the anchor bolts on east side of frame were snapped.

January 13

Cells shutdown at 0900 because product tanks M-104 and M-105 were full and large cell feed tank M-101 was empty due to front end shutdown for fan repair.

January 14

Plant restarted at 1100. No problems in front end or cell system.

January 15

A 22 hour loss analysis run was initiated with front end and cell system operating independently.

January 24

Plant shutdown occurred at 1400 hrs. Low cell area throughput and resultant low caustic inventory forced shutdown. Inspection of M-106 indicated the bottom packed section of Tellerettes had dropped into the drum.

January 28 - February 2, 1974

Repairs on pumps and partial cell rebuilding completed. Integrated plant operation started at 0930 on February 2.

February 6-7

Continuous operation interrupted for 17 hours due to shutdown of boiler #4.

February 16

Plant operation shut down at 0930 due to low feed liquor inventory. Installed line for continuous water addition to M-101.

February 18, 1974

Integrated plant operation restarted at 1100 hrs.

February 21

WEPCo boiler #4 shutdown caused shutdown of SO2 plant at 2015 hrs.

February 25

Integrated plant operation restarted at 1300 hrs.

February 26 - 27

EPA testing of absorption system being completed.

March 9, 1974

Plant shut down at 2100 hrs due to leaks in stripper OH piping.

March 12

Operation resumed at 1045 hrs after replacement of R-101 bearings.

March 15

The last test was completed at 0800. Plant continues to operate.

March 25 - April 8

Plant shut down for planned rebuilding of cell system at 0830 on March 25. Startup postponed from March 29 at WEPCo request due to boiler #4 shutdown and wet coal problems. Start of integrated operation on April 8 at 0800.

April 17

Plant shut down at 1300 hrs to repair stripper OH piping leak. Startup delayed by boiler #4 problems.

April 23

Integrated plant operation started at 1300 hrs.

April 26

Shutdown at 0200 caused by boiler #4 shutdown. Cell system restarted at 0500. Front end startup delayed by split rubber boot on G-101. Ready for startup at 1000 hrs but delayed at WEPCO request. Front end restarted at 1300 hrs.

April 30, 1974

Plant shutdown at 1400 hrs for planned repair and feed liquor makeup.

May 9

Plant restarted at 1600 hrs. Delay caused by off-spec caustic delivered and used in feed liquor makeup.

APPENDIX C

OXIDATION CALCULATIONS

A. Sample Calculation of Oxidation as Determined by Sodium Balance Method

Caustic Feed Rate to A-101 = 0.40 gpm
= 1.52 liters/min
Caustic Concentration = 1.85 N

Reactable sodium to A- 101 = (1.52) (1.85) = 2.82 g-ion/min

Analysis of Draw Liquor:

NaHSO = 1.30 g-mole/liter
Na2SO3 = 0.165 mole/liter

Reactable sodium in draw liquor in form of sulfite-bisulfite:

NaHSO = (1.30) (1.52) = 1.97 g-mole/min
Na2SO3 = (0.165) (1.52) (2) = 0.50 g-mole/min
2.47

Sodium disappearance - 2.82-2.47 = 0.37 g-ion/min
Sodium in form of sulfate = 0.37/2 = 0.185 g-ion/min

SO2 absorbed in liquid phase:

(1.30) (1.52) + (0.165) (1.52) + 0.185 = 2.405 g-mole/min

Therefore, oxidation is
(0.185/2.405) (100) = 7.8%

B. Sample Calculation of Oxidation as Determined by Ratio Method

Data: Gas Flow = 9,000 lb/hr
SO2 in = 1,075 ppm
out = 50 ppm
S/C = 0.90
(Sodium/sulfate) as determined by chemical analysis is 3.07
Caustic = 1.85 N sodium sulfate feed = 1.32 g-mole/liter

SO2 disappearance in gas phase:

(9,000 lb/hr) (1,075-50) ($14.9/10^6$) = 137.5 g-mole/hr

Assume Oxidation = 10%

NaHSO + Na2SO3 in draw = 0.90(137.5) = 123.5 g-mole/hr
Na2SO4 in draw = 137.5 - 123.5 = 14 g-mole/hr
Sodium with NaHSO3 - Na2SO3 = 123.5/0.90 = 137.5 g-mole/hr
Sodium with Na2SO4 = 14 (2) = 28.0 g-mole/hr

Total Sodium 165.5 g-mole/hr

Caustic flow to A-101 = 168.5/1.85 = 89.5 l/hr

Sodium Sulfate in = (89.5)(1.32) = 118 g-mole/hr

Sodium in Sodium Sulfate = 118(2) = 236 g-ion/hr

Sodium/Sulfate in Draw Liquor $\frac{236 + 165.5}{118 + 14}$ = 3.04

Sodium/Sulfate as measured = 3.07

Therefore, oxidation is slightly less than 10%.

C. Sample Calculation of Oxidation by Acid-Base Balance

Recycle Acid Feed Rate to Stripper = 0.90 gpm

Recycle Acid Concentration = 0.50 g-mole/l

pH Buffer Tank Feed Rate = 10.9 gallon/hr (average)

Let a = NaHSO3 = 1.30
b = Na2SO3 = 0.165
c = Na2SO4 = 3.07

$$S/C = \frac{a + b}{a + 2b} = 0.88$$

a/b = 7.88

Total acid addition =
(0.90)(3.78)(60)(0.50) = 102.1 g-mole/hr

Excess acid =
$(10.9)(3.78)\left(\frac{1.85}{2}\right)$ = 38 g-mole/hr

SO2 released =
$\frac{(7.88)}{(8.88)}(2)(64.1) + \frac{(64.1)}{(8.88)}$ = 121.0 g-mole/hr

Total gas phase SO2 disappearance =
137.5 g-mole/hr

Oxidation =
$\frac{137.5 - 121.0}{137.5}(100)$ = 12.0%

APPENDIX D
SULFUR REMOVAL CALCULATIONS

TOTAL GAS PHASE SULFUR DISAPPEARANCE

Gas flow = 8000 lb/hr
SO2 in = 1600
out = 200

Therefore SO2 removed = 24.0 lb/hr
= 170.0 g-mole/hr

SULFUR REMOVAL CALCULATIONS

METHOD I

Caustic Flow rate = 0.50 gpm

Caustic Analysis	gm/l	g-mole/l
NaOH	78	1.950
Na2SO4	200	1.408
Net Draw Analysis		
NaHSO	110	1.058
Na2SO3	20	0.159
Na2SO4	250	1.761

S/C = 0.884

Total Na in caustic = 4.766 g-mole/l
Total Na in net draw = 4.897 g-mole/l

∴ Net draw flow rate = 0.50 (4.766/4.897) = 0.487 gpm

Total sulfur appearance as SO2 = 0.487(60)(3.78)(1.058 + 0.159)
= 134.3 g-mole/hr

Total Na with sulfur as SO2 = 134.3/0.884 = 151.8 g-mole/hr

Total free Na in = 0.50(3.78)(60)(1.95) = 221.1 g-mole/hr

Sulfur appearance as Na2SO4 = (221.1 = 151.8)/2
= 34.7 g-mole/hr

Total liquid phase sulfur appearance = 34.7 + 134.3
= 169.0 g-mole/hr

METHOD II

Total sulfur appearance as SO_2 (as above) = 134.3 g-mole/hr

Sulfur appearance as Na_2SO_4 = $[(0.487)(1.761) - (0.50)(1.408)]\,3.78(60) = 34.8$ g-mole/hr

Total liquid phase sulfur appearance = 34.8 + 134.3
= 169.1 g-mole/hr.

APPENDIX E

BRITISH TO METRIC CONVERSION

To Convert from	To	Multiply by
acfm	mm^3/hr	1.70
ft	m	0.305
ft/sec	m/sec	0.305
g/mcf	l/m^3	0.134
gpm	l/min	3.79
gpm/ft^2	l/min/m	40.8
gr/scf	gr/m^3	2.29
in.	cm	2.54
in. H2O	mm Hg	1.87
lb-moles	gm-moles	4.54
lb-moles/hr	gm-moles/min	7.56
lb-moles/min	gm-moles/sec	7.56
°F	°C	Subtract 32 and Divide by 1.8

APPENDIX F

TABULAR SUMMARIES AND MEASUREMENTS

TABLE F-1

SUMMARY OF TEST RESULTS

				Quantity of SO_2 Removed		Caustic				
Test No.	SO_2 Inlet ppm	SO_2 Removal %	Gas Rate Lb/Hr	Gas Phase Dis. g mol/hr	Liquid Phase App. g mol/hr	Flow Gpm	Na Conc. g mol/L	Na to Absorber g mol/hr	$NaSO_4$ g mol/L	Circ. Rate Gpm
7	1,815	86.2	8,465	200	203.9	0.611	1.822	252.8	1.12	7
8		ABORT								
9		ABORT								
10	2,265	88.5	8,634	262	255.7	0.646	2.088	306.4	1.205	7
11	1,016	96.3	8,883	132	140.8	0.389	2.117	187.0	1.283	7
12	1,925	92.1	8,790	235	217.1	0.546	2.026	251.2	1.378	10
13	1,550	93.3	8,716	176.9	176.7	0.532	1.778	214.8	1.317	7
14	1,975	93.7	7,375	189.9	174.2	0.506	1.909	219.4	1.261	7
15	1,815	88.0	8,352	205.9	210.6	0.616	1.767	247.2	1.652	10
16		ABORT								
18	2,100	97.5	4,475	136.7	129.6	0.498	1.485	168.0	1.378	10
19		ABORT								
20	2,380	93.2	6,621	216.3	205.8	0.546	1.940	240.6	1.356	10
21	2,343	89.2	5,336	167.5	165.4	0.483	1.767	193.8	1.546	11.5
21*	2,370	89.0	5,320	170.2	167.6	0.490	1.781	198.2	1.536	11.5
22	2,098	87.5	4,499	123.4	126.6	0.367	1.879	156.6	1.749	11.5
23	2,164	84.5	5,360	145.9	151.3	0.406	1.981	182.7	1.798	10
24	2,026	89.2	7,886	213.5	219.2	0.638	1.812	262.6	1.561	11.5
25	2,020	90.0	7,930	214.8	228.1	0.606	2.110	290.4	1.498	11.5
26	1,693	88.4	7,666	170.8	171.5	0.490	1.992	221.7	1.609	11.5
27	1,732	90.2	7,555	176.7	177.0	0.513	1.998	232.8	1.578	30
28	2,682	92.9	6,481	241.7	250.6	0.647	2.070	304.2	1.681	10
29	2,328	91.0	6,334	196.9	199.0	0.522	2.097	248.6	1.540	10
30	2,924	90.4	6,373	249.9	268.8	0.644	2.154	315.1	1.534	10
31	3,071	91.4	5,834	234.9	252.1	0.627	2.079	296.1	1.475	10
32	3,640	93.4	4,880	257.0	278.8	0.731	1.994	331.1	1.488	10
33		ABORT								
34	2,068	89.3	8,093	226.9	235.7	0.716	1.778	289.1	1.258	7

TABLE F-1 (Continued)

SUMMARY OF TEST RESULTS

Test No.	Net Draw Liquor Analysis in GM/L			S/C	Fe in NaOH m g/L	Absorber Caustic Utilization SO_2/Na	Oxidation			Na Caustic / Na Net Draw	Notes
	Na_2SO_3	$NaHSO_3$	Na_2SO_4				Sodium Balance Method	Ratio Method	Overall Acid Method		
7	11.2	117.8	196.8	0.934	-	0.791	17.1	15.56	7.5*	0.988	
8											
9											
10	11.9	154.2	155.8	0.913	-	0.855	10.5	9.0	-	0.998	
11	24.7	133.5	208.5	0.883	-	0.706	12.8	11.5	-	1.003	
12	21.2	143.1	203.4	0.905	-	0.935	7.6	15.8	-	1.049	
13	18.4	120.6	205.6	0.899	-	0.823	10.4	10.2	-	1.011	
14	20.0	123.6	212.0	0.885	-	0.866	14.3	14.0	-	0.977	
15	18.6	141.2	261.0	0.910	-	0.833	7.02	7.0	-	0.955	
16											
18	23.5	95.3	240.5	0.851	0.65	0.814	15.8	8.6	-	0.931	
19											
20	10.9	141.8	230.7	0.936	0.15	0.899	14.1	14.8	-	0.989	
21	11.6	136.8	253.5	0.940	0.70	0.864	10.8	11.3	-	0.964	
21*	9.7	133.7	255.6	0.947	0.70	0.859	13.1	13.0	22.3/20.9	0.963	Loss analysis run - part of run 21
22	9.2	121.1	290	0.94	2.90	0.783	18.3	18.3	26.1/30.8*	1.001	
23	9.7	138.0	295.9	0.950	1.40	0.799	16.0	15.9	-	0.985	
24	12.3	128.9	250.8	0.927	0.40	0.813	12.4	12.1	23.1	1.561	
25	18.7	135.1	271.5	0.907	0.35	0.739	18.6	17.9	-	1.489	Split caustic flow
26	13.0	123.4	293.6	0.930	0.20	0.770	22.2	21.5	28.9	0.938	Split caustic flow
27	9.6	115.5	289.8	0.928	0.29	0.759	25.2	24.2	18.5	0.955	High liquid circulation rate
28	13.5	142.7	280.0	0.93	0.47	0.795	15.1	14.8	24.1	0.983	
29	20.7	149.1	277.0	0.909	0.13	0.792	14.7	12.1	14.0	0.908	
30	9.7	170.9	253.7	0.953	0.25	0.793	10.7	8.9	8.0	0.962	
31	12.0	170.1	245.8	0.930	0.31	0.793	9.4	8.7	15.7	0.939	
32	7.8	164.1	249.3	0.943	0.09	0.776	10.2	8.4	-	0.936	
33											
34	11.2	132.0	216.8	0.926	0.32	0.785	13.1	12.4	23.0*	0.945	

*Questionable acid flow measurement

TABLE F-2

DISTRIBUTION OF OXIDATION AND SO_2 REMOVAL BETWEEN TOP AND BOTTOM ABSORPTION STAGES

	Average for Run				Overall Oxidation		Stage 1 (Bottom)			
Run	Inlet SO_2 ppm	Gas Rate Lb/Hr	NO_2SO_4 in NaOH g mol/L	SO_2 Removed g mol Min	% Oxidation	SO_4 Formed g mol/min	S/C	SO_2 Removed g mol/min	SO_4 Formed g mol/min	% Oxidation
10-1	2,265	8,634	1.205	4.43	6.5	.288	.898	.26	.071	27.0
10-5				4.20	11.0	.462	.925	.50	.103	20.7
13-5	1,550	8,716	1.317	2.92	9.5	.277	.882	.02	.128	100+
13-9				2.76	13.6	.376	.918	.08	.194	100+
20-1	2,413	6,429	1.345	3.76	16.8	.632	.966	.87	.245	28.1
20-4				3.68	16.1	.592	.927	.47	.306	65.6
21-11	2,343	5,336	1.546	3.04	11.0	.335	.945	.36	.161	43.9
21-16				2.62	14.6	.383	.941	.30	.230	75.8
26-3	1,724	7,666	1.628	2.52	24.0	.605	.924	1.32	.427	32.2
26-5				2.90	19.3	.559	.930	1.55	.402	26.0
26-8				2.87	22.0	.631	.920	1.73	.430	24.8
28-3	2,669	6,479	1.674	3.98	20.3	.809	.931	.50	.398	79.6
28-5				4.17	14.2	.591	.936	.45	.264	58.9
29-10	2,328	6,334	1.540	3.21	9.2	.297	.907	.23	.065	28.3
31-11	3,050	5,689	1.475	3.80	8.6	.327	.940	.27	.161	60.0
31-14				4.18	10.2	.426	.944	.30	.147	49.0

TABLE F-2 (Continued)

DISTRIBUTION OF OXIDATION AND SO_2 REMOVAL BETWEEN TOP AND BOTTOM ABSORPTION STAGES

	Stage 2 (Top)						Stage 1			Stage 2		
Run	S/C	SO_2 Removed g mol/min	SO_4 Formed g mol/min	% Oxidation	% of Removal Stage(2)	% of Oxidation Stage(2)	Na_2SO_3	NaH SO_3	Na_2SO_4	Na_2SO_3	NaH SO_3	Na_2SO_4
10-1	.840	4.17	.217	5.2	94.1	75.3	25.2	161.9	206	39.7	139.5	198
10-5	.828	3.70	.359	9.7	88.1	77.7	9.2	143.1	186	27.7	127.0	183
13-5	.833	2.90	.119	4.1	99.5	43.0	20.5	109.8	211	32.8	108.3	205
13-9	.781	2.68	.182	6.8	96.9	48.4	14.6	123.9	211	44.1	93.7	190
20-1	.820	2.89	.387	13.4	76.8	61.1	3.2	143.2	220.6	20.3	117.1	222.4
20-4	.811	3.21	.286	8.9	87.3	48.1	11.4	139.5	242	38.0	111.8	212
21-11	.799	2.68	.174	6.5	88.0	52.0	10.8	130.7	244	44.9	110.3	242
21-16	.825	2.32	.153	6.6	88.4	40.0	10.2	127.5	288	35.8	109.7	267
26-3	.766	1.20	.178	14.8	47.4	29.4	9.0	117.8	288	48.6	90.9	268
26-5	.772	1.35	.157	11.6	46.7	28.1	12.6	127.5	282	47.7	98.3	259
26-8	.738	1.14	.201	17.7	39.6	31.7	14.2	123.3	300	53.2	84.1	291
28-3	.726	3.48	.411	11.8	87.1	50.8	11.2	137.3	316	66.1	89.7	294
28-5	.773	3.72	.327	8.8	89.2	55.0	12.2	142.8	271	50.3	105.8	260
29-10	.762	2.98	.232	7.8	92.7	54.6	20.8	149.85	257	59.8	108.4	253
31-11	.743	3.53	.166	4.7	92.9	51.0	8.8	173.3	242	67.0	104.8	233
31-14	.775	3.88	.279	7.2	92.8	65.5	7.4	172.3	244	60.9	113.1	238

TABLE F-3A

OVERALL GAS MASS TRANSFER COEFFICIENTS FOR SO_2 ABSORPTION IN SODIUM SULFITE-SODIUM BISULFITE SOLUTIONS

Run	SO_2 Inlet ppm Dry	% Removed Overall	Percent Oxidation Total	SO_2 Removed g mol/min	App g mol Min
10-1	2,400	87.0	6.5	4.43	4.37
10-5	2,250	86.5	11.0	4.20	3.96
13-5	1,560	86.5	9.5	2.92	2.92
13-9	1,508	93.4	13.6	2.76	2.92
20-1	2,490	95.2	16.8	3.76	3.48
20-4	2,310	89.6	16.1	3.68	3.43
21-11	2,520	91.1	11.0	3.04	2.92
21-16	2,150	84.0	14.6	2.62	2.40
26-3	1,560	83.7	24.0	2.52	2.55
26-5	1,680	89.3	19.3	2.90	2.97
26-8	1,650	92.7	22.0	2.87	2.96
28-3	2,514	94.4	20.3	3.98	3.17
28-5	2,835	92.6	14.2	4.17	3.62
29-10	2,310	87.9	9.2	3.183	3.303
31-11	2,880	95.8	8.6	3.80	4.19
31-14	3,053	89.4	10.2	4.18	4.44

TABLE F-3B

OVERALL GAS MASS TRANSFER COEFFICIENTS FOR SO_2 ABSORPTION

IN SODIUM SULFITE-SODIUM BISULFITE SOLUTIONS

	Stage One (Bottom)											
Run	S/C Btm	pp SO_2 mm Hg	x 10^4 Ye Btm	S/C Top	pp SO_2 Top mm Hg	x 10^4 Ye Top	SO_2 Rem g mol Min	Fraction Removed	x 10^4 Y Btm	Y Top	NO_G	HO_G
10-1	.898	0.67	8.8	.893	0.67	8.8	0.26	.059	21.1	20.0	.094	106.7
10-5	.925	1.05	13.8	.834	0.225	3.0	0.50	.119	19.8	17.8	.205	48.7
13-5	.882	0.50	6.6	.838	0.240	3.2	0.02	.007	13.7	13.6	.012	864.5
13-9	.918	0.92	12.1	.908	0.76	10.0	0.08	.027	13.3	12.9	.208	48.2
20-1	.966	2.00	26.4	.956	1.70	22.4	0.87	.231	21.9	17.1	-	-
20-4	.927	1.06	14.0	.919	0.92	12.1	0.47	.128	20.3	18.0	.377	26.5
21-11	.945	1.43	18.8	.937	1.24	16.3	0.36	.118	22.2	19.8	.696	14.4
21-16	.941	1.34	17.7	.936	1.22	16.1	0.30	.115	18.9	17.1	1.64	6.1
26-3	.924	1.04	13.7	.889	0.56	7.4	1.32	.524	13.7	7.7	3.15	3.17
26-5	.930	1.10	14.5	.897	0.66	8.7	1.55	.534	14.8	7.7	-	-
26-8	.920	0.95	12.5	.885	0.53	7.0	1.73	.603	14.5	6.4	-	-
28-3	.931	1.12	14.8	.915	0.87	11.4	0.50	.126	22.1	19.5	.338	29.6
28-5	.936	1.24	16.3	.924	1.00	13.2	0.45	.108	25.0	22.6	.278	36.0
29-10	.907	0.76	10.0	.899	0.69	9.1	0.23	.072	20.3	19.0	.123	81.4
31-11	.940	1.30	17.1	.931	1.20	15.8	0.27	.071	25.4	23.6	.224	44.7
31-14	.944	1.41	18.6	.931	1.20	15.8	0.30	.072	26.9	25.1	.205	48.8

TABLE F-3C

OVERALL GAS MASS TRANSFER COEFFICIENTS FOR SO_2 ABSORPTION IN SODIUM SULFITE-SODIUM BISULFITE SOLUTIONS

	Stage Two (Top)											
Run	S/C Btm	pp SO_2 Btm	$\times 10^4$ Ye Btm	S/C Top	pp SO_2 Top	$\times 10^4$ Ye Top	SO_2 Rem g mol Min	Fraction Removed	Y Btm	Y Top	NO_G	HO_G
10-1	.840	0.25	3.3	.765	0.071	0.9	4.17	.941	20.0	2.7	2.59	3.87
10-5	.828	0.21	2.8	.782	0.093	1.2	3.70	.881	17.8	2.7	2.58	3.88
13-5	.833	0.225	3.0	.768	0.075	1.0	2.90	.993	13.6	1.9	2.97	3.36
13-9	.781	0.105	1.4	.721	0.034	0.5	2.68	.973	12.9	0.9	3.63	2.75
20-1	.889	0.57	7.5	.830	0.21	2.8	2.89	.769	17.1	1.1	-	-
20-4	.820	0.18	2.4	.770	0.077	1.0	3.21	.872	18.0	2.1	2.91	3.44
21-11	.799	0.126	1.7	.765	0.071	0.9	2.68	.882	19.8	2.0	2.93	3.41
21-16	.825	0.195	2.6	.792	0.11	1.4	2.32	.885	17.1	3.0	2.41	4.15
26-3	.766	0.072	0.9	.748	0.053	0.7	1.20	.476	7.7	2.2	1.57	6.38
26-5	.772	0.080	1.1	.758	0.063	0.8	1.35	.466	7.7	1.6	2.22	4.51
26-8	.738	0.046	0.6	.728	0.038	0.5	1.14	.397	6.4	1.1	2.31	4.32
28-3	.726	0.037	0.5	.678	0.017	0.2	3.48	.834	19.5	1.2	2.99	3.34
28-5	.773	0.080	1.1	.726	0.037	0.5	3.72	.892	22.5	1.9	2.81	3.56
29-10	.762	0.067	0.9	.723	0.035	0.5	2.98	.928	19.0	2.5		
31-11	.743	0.049	0.6	.700	0.024	0.3	3.53	.929	23.6	1.1	3.41	2.94
31-14	.775	0.084	1.1	.716	0.031	0.4	3.88	.928	25.1	2.9	2.34	4.28

TABLE F-4

SUMMARY OF MAJOR STREAM METALS ANALYSIS

Sample No.	54	64		62	241	242	243	244	245	246	247	248	349	350	381	382
Location	Net Draw	Net Draw	Acid	Strip Btms	A Anolyte	B Anolyte	Mid Anolyte	Comb Catholyte	Cell Feed At Stks	Net Draw	Strip Btms	Quench H_2O Return	Cell Feed T-1	Cell Feed At Stks	Strip Btms	Quench H_2O Return
Date	7/7	7/7	7/16	7/7	8/22	8/22	8/22	8/22	8/22	8/22	8/22	8/22	10/5	10/5	10/27	10/27
Time	0100	1530		0700	1535	1535	1535	1535	1535	1600	1600	1600	1600	1600	1320	1320
Cations:																
Mn	0.2	0.5	0.1	0.2	0.30	0.06	0.36	0.23	1.35	0.35	0.60	0.15	0.25	1.50	2.0	0.1
Mg	<1.	3.	1.	<1.	2.0	<1.	<1.	<1.	2.	10.	5.	38.	0.60	0.65	0.62	34.
K	70	75	60	55	145	0.6	130	400	170	250	175	4.0				
Al	<0.5	5.0	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.6	0.5	<0.5				
Pb	2.5	3.0	8.0	2.0	5.6	3.8	1.5	1.7	1.4	2.0	3.5	<0.02				
Zn	0.5	1.0	1.0	0.5	0.63	0.28	0.56	0.54	0.58	0.68	0.62	<0.02				
Cr	7.0	8.0	6.0	5.0	0.21	<0.02	0.10	0.15	0.12	0.63	0.43	1.0	0.14	0.14		
Ca	2.5	13.0	7.0	7.0	5.2	0.5	5.6	1.3	5.6	5.3	6.3	52.0	3.3	3.0	7.8	77.5
Na	100,000	100,000	50,000	75,000	45,000	15.	43,800	90,000	51,000	65,000	50,000	30	54,000	55,000	73,400	24.
*Fe Limnetics	4.0	4.5	2.0	2.0	1.8	2.0	1.4	1.8	1.6	3.6	58.0	3.6	3.2	3.1	33	1.7
WEPCO					1.9	0.4	1.6	2.2	1.8	2.4	2.1	0.3				
Ni																
Cu																
Co																
Mo													<0.05	<0.05		
Nitrites					0.004	0.004	0.004	<0.002	<0.002	<0.002	0.006	0.012				
Nitrates					130	110	18	30	29	<0.01	13	0.8				
Cl					152		698	161.5	741	29,000	950	152	10.5	9.3	1.2	<1.
Si					36	6	29	31	29	23	33	6			20	8
Chemical Analysis:																
$NaHSO_3$ g/l	Nil	52.1								64.5						
Na_2SO_3 g/l	26.3	19.6							0.15	45.5						
Na_2SO_4 g/l				171	140.5	0	151	125	176	143	174					
NaOH g/l	Nil							108								
H_2SO_4 g/l					39.2	100	9.8				1.2	0.30			5.4	0.98
pH	9.0	6.1		8.9	1.0	1.0	1.2	13.	8.85	5.75	2.35	2.25			2.3	3.1
p 60 °C	1.20	1.20		1.16	1.125	1.048	1.116	1.184	1.1335	1.1655		0.9884			1.166	0.991

*Limnetics Fe Analysis proven incorrect

TABLE F-4 (Continued)

SUMMARY OF MAJOR STREAM METALS ANALYSIS

Sample No.	383	384	385	386	387	388	389	902	903	904	905	906	907	908	909	
Location	Net Draw	Cell Feed T-1	Mid Anolyte	Comb Catholyte	Cell Feed At Stks	B Anolyte	A Anolyte	Net Draw	Quench H_2O Return	Strip Btms	Comb Catholyte	B Anolyte	A Anolyte	Mid Anolyte	Cell Feed At Stks	Cell Feed At Stks
Date	10/27	10/27	10/27	10/27	10/27	10/27	10/27	1/8	1/8	1/8	1/8	1/8	1/8	1/8	1/8	2/28
Time	1320	1320	1320	1320	1320	1320	1320	0730	0730	0730	0730	0730	0730	0730	0730	1600
Cations:																
Mn	0.8	1.7	1.4	0.5	6.2	0.8	2.0	1.6	0.13	1.3	1.0	0.25	1.1	0.9	1.0	0.18
Mg	0.44	0.58	0.47	0.13	0.59	0.40	0.41	0.36	51.	0.48	0.15	0.25	0.32	0.30	0.38	0.40
K																
Al																0.2
Pb								0.2	0.4	4.0	0.5	2.0	6.0	4.0	2.0	2.0
Zn																0.51
Cr																<0.1
Ca	7.1	7.2	6.0	5.2	7.3	2.1	5.9	10.5	105.	10.5	8.8	3.2	8.3	10.0	10.5	3.4
Na	85,000	70,000	37,500	96,800	75,000	1,250	422,000	104,000	110	79,000	100,000	13,000	60,000	60,000	72,000	
*Fe Limnetics/WEPCO	4.8	3.9	3.3	4.3	3.8	1.5	3.2	.7/.5	1.5/1.6	1.1/1.5	0.3/0.1	0.5/<.01	0.7/<.01	0.7/<.01	0.3/<.01	<0.5/<.01
Ni								<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	4.0
Cu								<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	0.6
Co								<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	<0.1
Mo																
Nitrites																
Nitrates																
Cl	352	<1.	5.8	<1.	<1.	<1.	<1.	-	224	122	-	11.6	55.2	105	134	
Si	14	16	16	28	16	0.06	0.16	6	14.8	6.3	95.9	11.2	6.9	13.3	12.1	
Chemical Analysis:																
$NaHSO_3$ g/l	124.8	1.04						148.4								
Na_2SO_3 g/l	7.0	1.89			0.10			22.95								
Na_2SO_4 g/l				180	218	46.4	173	229	7	236.4	186	52.7	191.8	186.6	230	
NaOH g/l				80.8							78.20					
H_2SO_4 g/l			20.6			97.5	45.		0.98	10.09	-	92.00	44.28	25.83	-	
pH	5.4	8.1	1.9	12.9	8.8			4.9	2.3	1.9	12.8	0.05	1.1	1.4	7.5	
ρ 60 °C	1.208	1.168		1.201	1.167	1.081	1.157	1.160	1.0	1.183	1.210	1.079	1.162	1.151	1.180	

*Limnetics Fe Analysis proven incorrect

TABLE F-5

SUMMARY - MATERIALS OF CONSTRUCTION TESTING

Spool No.	1		2		3		4	
Environment	Flue Gas Quench Section (Cooling H_2O With pH 2.5) Aeration: Moderate Spool Located Near Bottom of Section, Covered With Liquid 100% of Time Periodic Operation - System Drained and Flushed When Shutdown Occurred		Absorber (Bisulfite Solution pH 5.5 $NaHSO_3$ @ 100 g/L; $NaSO_3$ @ 10 g/L; Na_2SO_4 @ 200 g/L Spool Located on Top of Packing, Therefore Exposed to Spray of Process Solution Periodic Operation - System Drained and Flushed When Shutdown Occurred		Stripper Overhead (Wet SO_2 With Some Na_2SO_4 From Entrainment (Vapor Phase) Spool Located in Vapor Phase Just Below Condenser Periodic Operation - System Drained and Flushed When Shutdown Occurred		Stripper Reboiler (23% Wt Na_2SO_4 Solution With 0.04 to 0.1 N H_2SO_4; pH = 2.0 to 2.5) Spool Located in Stripper Reboiler Drum (On Bottom) Periodic Operation - System Drained and Flushed When Shutdown Occurred	
	Temp: 120 F Avg (110-130 F) Exposure Time: 2,300 Hr		Temp: 110 Avg (100-120 F) Exposure Time: 1,900 Hr Extensive Aeration		Temp: 230 F Avg (220-240 F) Exposure Time: 2,300 Hr		Temp: 230 F Avg (225-245 F) Exposure Time: 2,300 Hr	
Test Results	Coupon Material	Corrosion Rate (mpy)	Coupon Material	Corrosion Rate (mpy)	Coupon Material	Corrosion Rate (mpy)	Coupon Material	Corrosion Rate (mpy)
	Incoloy 825	0.1**	Allegheny Ludlum 6X	0.0	Carpenter 20Cb-3	0.1	Incoloy 825	0.1
	Incoloy 825	0.1**	Allegheny Ludlum 6X	0.0	Carpenter 20Cb-3	0.1	Incoloy 825	0.1
	Type 316 S.S.	0.1*	Incoloy 825	0.1	Hastelloy G	0.2*	Carpenter 20Cb-3	14.9*
	Type 316 S.S.	0.1*	Incoloy 825	0.0	Hastelloy G	0.3	Carpenter 20Cb-3	0.1
	Carpenter 20Cb-3	0.1	Durimet 20	0.0*	Type 316 S.S.	0.2**	Durimet 20	12.2**
	Carpenter 20Cb-3	0.1	Durimet 20	0.1*	Type 316 S.S.	0.1	Durimet 20	18.7**
	Hastelloy G	0.1	Type 316 S.S.	0.1***	Incoloy 825	0.1	Titanium	0.0
	Hastelloy G	0.1	Type 316 S.S.	0.1***			Titanium	0.0
	Titanium - 0.2% Palladium	0.1	Carpenter 20Cb-3	0.1*				
			Carpenter 20Cb-3	0.1*				
	Titanium - 0.2% Palladium	0.1	Chlorimet 2	22.1**				
			Chlorimet 2	23.0**				
	*Incipient pitting **Few random incipient pits (1 mil diam and depth)		*Incipient pitting **Intergranular etch ***Numerous small shallow pits		*Incipient crevice corrosion **Random pits		*Crevice corrosion up to 8 mils deep **Intergranular etch	

TABLE F-5 (Continued)

SUMMARY - MATERIALS OF CONSTRUCTION TESTING

Spool No.	5		6		7	
Environment	Feed Liquor Tank (Na_2SO_4 Solution, 200 to 280 g/L in DI H_2O, pH = 8.0 - 8.5) Spool Located Just Off Floor of Vessel. Subjected to Both Acid and Base Conditions (pH 1.0 and 13+) and Temp 150 F on Na_2SO_4 Makeup		Caustic Storage Tank (2.0 N NaOh Solution Plus 17% Wt Na_2SO_4) Spool Located on Floor of Tank; Always in Liquid Phase		Acid Storage Tank (1.0 N H_2SO_4 Solution Plus 17% Wt Na_2SO_4) Spool Located on Floor of Vessel; Always in Liquid Phase	
	Temp: 100 F Avg (90-110 F) Exposure Time: 81 Days		Temp: 120 F Avg (100-140 F) Exposure Time: 218 Days		Temp: 120 F Avg (100-140 F) Exposure Time: 218 Days	
Test Results	Coupon Material	Corrosion Rate (mpy)	Coupon Material	Corrosion Rate (mpy)	Coupon Material	Corrosion Rate (mpy)
	Incoloy 825	0.0	Inconel 600	0.0	Type 317 S.S.	0.0*
	Incoloy 825	0.0	Inconel 600	0.0	Type 317 S.S.	0.0
	Carbon Steel 1010	4.6*	Carbon Steel 1010	0.1	Incoloy 825	0.0
	Carbon Steel 1010	417	Carbon Steel 1010	0.1	Incoloy 825	0.0
			Monel 400	0.3	Durimet 20	0.0
			Monel 400	0.3	Durimet 20	0.0
			Nickel 200	0.3	Carpenter 20Cb-3	0.0
			Nickel 200	0.2	Carpenter 20Cb-3	0.0
					Hastelloy G	0.0
					Hastelloy G	0.0
					Type 316 S.S.	0.0
					Type 316 S.S.	0.0
					Allegheny Ludlum 6X	0.1
					Allegheny Ludlum 6X	0.1
					Chlorimet 2	104.8**
					Chlorimet 2	86.5**

*Nonuniform general corrosion; broad pits

*A few random pits 1 mil deep

**Intergranular etch; one piece partially corroded away

APPENDIX G
IGT TRACE IRON ANALYSIS

IGT

INSTITUTE OF GAS TECHNOLOGY • 3424 SOUTH STATE STREET • IIT CENTER • CHICAGO, ILLINOIS 60616
PHONE 225-9600 AREA CODE 312

February 4, 1974

Mr. Alex Korosi
Stone and Webster Engineering Corp.
225 Franklin Street
Boston, Mass. 02107

Dear Alex:

This is the final report on the analytical work which was undertaken by our laboratories in order to resolve the problems associated with the trace iron determination of your "Wisconsin SO_2 Pilot Plant" scrubbing solutions.

The presence of high concentration of Na_2SO_4 (approx. 3 N) in your 8 sample solutions seriously interferred with the iron analysis by either atomic absorption or colorimetric methods. We therefore made up a series of synthetic samples containing known amounts of iron in Na_2SO_4 solutions to study the best way of arriving at a suitable method of analysis. The following comments and conclusions help to explain the significance of the results of Table 1 below.

Table 1.

CONCENTRATION OF IRON IN SAMPLES OF SODIUM SULFATE SOLUTIONS TAKEN FROM WISCONSIN SO_2 PILOT PLANT

Sample Identification	Iron, μg/ml By AA	Iron, μg/ml By Ferrozine
584	0.04	0.54
585	0.01	0.58
586	0.10	0.64
587	< 0.01	0.74
588	35	46
589	1.4	1.9
No. 1	3.3	3.9
No. 3A	0.48	1.0

I. Atomic Absorption Methods

A. Direct aspiration of the original 3N Na_2SO_4 solutions resulted in highly erratic iron values, but by diluting the samples with 4 to 5 parts of water (approx. 0.60 to 0.75 N in Na_2SO_4) and using a 3-slot burner head we were able to obtain results which were within ±5 % for up to 10μg/ml of iron present.

B. A solvent extraction scheme (Appendix 1) for iron with subsequent AA analysis of the solvent afforded the best set of values (Table 1) for iron, as judged by the complete recovery of known amounts of iron from a series of standard solutions.

II. Colorimetric Methods

A. The use of 1, 10-phenanthroline as colorimetric reagent for iron in 3 N Na_2SO_4 solutions again proved unworkable, since the high sulfate ion concentration caused considerable deviation from Beer's law. Dilution of the salt solutions reduced the deviation but the method did not have enough sensitivity for low iron concentrations.

B. Ferrozine, which is a relatively new colorimetric reagent for iron, forms an iron complex possessing 2.5 times the molar absorptivity of the similar iron 1, 10-phenanthroline complex. Because of this enhanced sensitivity and better tolerance for sulfate ion concentration, ferrozine gave much better results for iron in diluted solutions of Na_2SO_4 (not over 0.3 N) than the comparable 1, 10-phenanthroline procedure. Neither reagent, however, is as specific for iron as is the AA method, due to the formation of other metal iron complexes such as copper and cobalt.

Our conclusion, based on the above work, is that while atomic absorption method for dilute solutions of Na_2SO_4 (not to exceed 0.5 to 0.7 N) is workable, it is not as dependable as the solvent extraction - AA procedure for trace iron analysis in your system.

As a second choice ferrozine method of colorimetry may fill a limited function as a quality control measure provided that the Na_2SO_4 concentration in the analysis solution does not exceed 0.3 N and the operator keeps a watchful eye on the other metal ions and corrosion products which may give a positive or negative error.

Best regards.

Sincerely yours,

Andy

A. Attari
Manager, Analytical
Services

aa/ah
encl.

Appendix 1.

AA DETERMINATION OF TRACE IRON BY SOLVENT EXTRACTION OF IRON FROM 3N Na_2SO_4 SOLUTION

Reagents:

1. APCD soln.: 1g ammonium pyrrolidinecarbodithioate in 25 ml. water. Must be prepared fresh daily.

2. Ammonium acetate buffer, 5M: dissolve 385 g NH_4OAc in water, make to one liter.

3. Standard Fe soln.: dissolve one g. iron in 6N Hcl, make to one liter (1000μ g/ml).

Procedure:

a. Place a suitable aliquot of sample or standard solution, containing less than 10 μ g iron in less than 25 ml soln.

b. Add 2 ml 5M NH_4OAc soln., and sufficient NH_4OH or Hcl to bring the pH to 3.0 ± 0.1 with a pH meter.

c c. Transfer the soln. to a 50 ml volumetric flask, add 1 ml of APCD soln. to sample solution.

d. Add 5 ml methylisobutyl ketone (MIBK) and shake vigorously for one minute. Add water to bring the organic phase into the neck of the flask and aspirate directly from the flask for AA determinations.

PHASE 1B

DESIGN, FABRICATION, AND PERFORMANCE OF THE IONICS PROTOTYPE ELECTROLYTIC CELLS FOR THE STONE & WEBSTER/IONICS SO2 REMOVAL AND RECOVERY PROCESS

I

ABSTRACT - PHASE IB

Phase IB of the EPA-WEPCO sponsored program to evaluate the Stone & Webster/Ionics closed cycle SO2 removal system has been successfully completed. In this phase, prototype electrolytic cells, Types "A" and "B", having production capacities per cell more than five times those of the pilot plant size cells were developed. The performance of both types of cells was demonstrated; they meet the contract performance objectives for energy consumption per unit of caustic produced as well as, in the case of "B" cells, the current efficiency for purge sulfuric acid. A "cell package" concept in which cell membranes, diaphragms, screen separators, and molded rubber gaskets for two cells are preassembled was utilized to simplify field assembly of the cells.

II

CONCLUSIONS

1. The targeted performance objectives for both prototype "A" and "B" cells were satisfied in the current density range of 120 to 160 ampere per square foot (ASF) studied.

   The d-c energy in kilowatt-hours per pound of caustic produced at 160 ASF was under 2.47 for the prototype "A" cells and under 2.68 for the prototype "B" cells.

2. The production capacity per cell was increased by more than a factor of five over the 8 x 17 in. cells used in the WEPCO pilot plant, at the same electrical energy consumption.

3. In the case of prototype "B" cells, some internal and external leakage experienced initially was corrected by manual modification of the molded components. These modifications can be incorporated into the component molds.

4. The "cell package" concept was demonstrated in the prototype cells. A preassembled "cell package" contains the membranes, diaphragms, screen separators, and molded rubber gaskets for two cells. This innovation simplified the field assembly of the cells.

5. The prototype "A" and "B" cells are ready to be demonstrated in a larger scale operation.

III

RECOMMENDATIONS

1. The prototype "A" and "B" cells should be tested next on the 75 megawatt demonstration plant proposed under Phase II of this Contract.

2. Superficial modifications to the component molds, deemed desirable as a result of the prototype cell tests, should be made when manufacture of cells for a demonstration plant is undertaken.

IV

INTRODUCTION

The objectives of Phase IB of the program were to provide detailed operating test data on commercial prototypes of both 3-compartment (Type A) and 4-compartment (Type B) cells.

Phase IB was divided into three subphases: 1) Design and fabrication of the prototype cell components; 2) Design and fabrication of a facility to test the prototype cells; and 3) Operating tests and data reduction. These are discussed in the following sections of the report.

V

DESIGN AND FABRICATION OF THE PROTOTYPE CELL COMPONENTS

The design objectives were:

1. To increase the production capacity per cell by a factor of five at the same energy factor as the 8 x 17 in. cells used in the WEPCO pilot plant.

2. To maintain an internal cell height close to the 17 in. cell compartment height used in the "tall cell pilot plant."

3. To obtain good flow distribution within cells and between cells.

4. To simplify the field assembly of the cells.

5. To avoid exposure of the electrodes to the process solutions in the cell manifolds.

The production capacity was increased simply by increasing the effective area of the cells from 0.945 sq ft in the "tall cell pilot plant" to 5 sq ft in the prototype cells. The effective area ratio increase of 5/0.945 = 5.29 results in a d-c current equally higher at a given current density. The production capacity is directly proportional to the current.

The increase in area was achieved by widening the cells from 8 in. to a nominal 36 in. in the prototype cell. The internal compartment height is 20 in.

The current efficiency for electrolytic regeneration depends on good flow distribution. This was accomplished by using dual ports to feed and exhaust the major cell compartments, and by equipping selected ports with flow distribution channels. The components are shown in detail in the drawings listed in Table 5.1.

To obtain the same electrical energy consumption as in the tall cell pilot plant the same intercomponent distances have been maintained in the prototype cell. The flow rate of anolyte recirculation was increased by a factor of 5.29 per cell to achieve the same gas disengagement from the electrode compartment as in the "tall cell." A similar increase in catholyte recirculation flow rate was provided.

The field assembly of the cell was simplified by preassemblying the components into "cell packages." A "cell package" contains the membranes, diaphragms, screen separators, and molded rubber gaskets for two cells. Each unit in the package is held together by plastic rivets. The cell package is

TABLE 5.1

LIST OF DRAWINGS OF PROTOTYPE CELL COMPONENTS

Drawing No.*	Title
20043-SH1-8	Cathode Frame
20043-SH2-7	Cathode Frame Sections
20044-5	Cathode Insert
20045-SH1-8	Anode Frame
20045-SH2-8	Anode Frame Sections
20046-6	Anode Insert
20047-SH1-5	Mid-Anolyte Compartment - Anode Side
20047-SH2-5	Mid-Anolyte Compartment - Cathode Side
20048-SH1-5	Center Compartment Frame - Anode Side
20048-SH2-7	Center Compartment Frame - Cathode Side
20049-4	Anode-Cathode Current Collector
20050-5	Anode
20051-5	Cathode
20052-5	Anode Screen-Cathode Side
20053-4	Mid-Anolyte Screen Cathode Side
20054-4	Mid-Catholyte Screen Compartment - Cathode Side
20066-2	Cell Assembly
20067-4	Flow Diagram-Sulfomat (5 ft^2) Test Facility
20068-2	"B" Cell Extrusion
20069-2	Package Retainer Rivet
20071-4	Hydraulic End Block
20077-2	Anode Diaphragm
20078-2	Cathode Diaphragm
20079-2	Anion Membrane
20080-2	Cation Membrane
20086-1	Cathode Subassembly Layout
20087-3	Anolyte Outlet Flow Distributor
20088-3	Anolyte Inlet Flow Distributor
20089-1	"B" Cell CC Frame Tab Spacer
20090-1	Anode Support Fingers
20092-1	Hydraulic Module Separator

*Drawings available upon request

hung over the rigid anode frame component with one cell on one side of the anode, and the other on the opposite side. For a module of eight cells, there are four anode frames, four cell packages, and five cathode frames. The rigid cathode frames are placed between the cell units that hang from the opposite anodes. Therefore, cell assembly is fast and the assembler is not concerned with individual membranes, diaphragms, and gaskets.

The electrode frames are molded from filled polypropylene and are similar to filter press components (Figure 5.1). The electrodes fit in from the side and are sealed in place by a filled polypropylene insert welded over the opening for the electrode. The electrode does not traverse any place in the frame where there are manifold holes that distribute the flows to and from the individual cells. Thus, exposure of the electrodes to the manifold electrolytes is not possible. The rididity of the electrode frames imparts equal rigidity and strength to the assembled module.

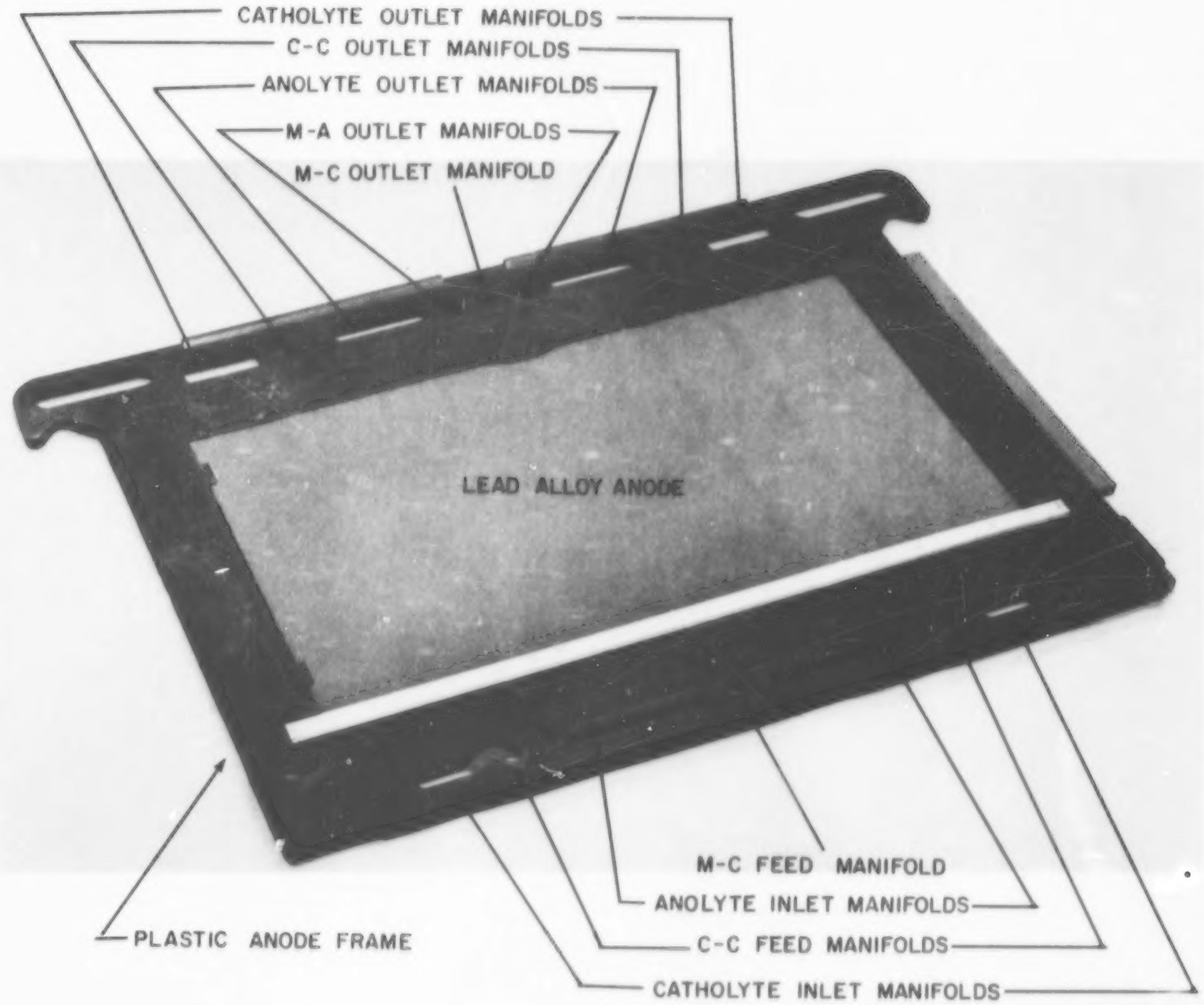

CATHOLYTE OUTLET MANIFOLDS
C-C OUTLET MANIFOLDS
ANOLYTE OUTLET MANIFOLDS
M-A OUTLET MANIFOLDS
M-C OUTLET MANIFOLD
LEAD ALLOY ANODE
PLASTIC ANODE FRAME
M-C FEED MANIFOLD
ANOLYTE INLET MANIFOLDS
C-C FEED MANIFOLDS
CATHOLYTE INLET MANIFOLDS

FIGURE 5.1 CELL ANODE ASSEMBLY

VI

PROTOTYPE CELL TEST FACILITY

The prototype cells were tested in a pilot facility constructed in Watertown. The test facility was designed to test sixteen "A" cells or sixteen "B" cells at a time at current densities up to 160 amperes per square foot of effective electrode area (ASF). As stated previously, each prototype cell has an effective electrode area of 5 sq ft.

The sixteen cells (either "A" or "B" cells) were arranged in two groups of eight cells each. The cells within a group ("electric module") were connected in parallel electrically. The two electric modules were connected in series. Hydraulically, all sixteen cells were connected in parallel (Figure 6.1).

The design caustic and acid production rates for the 16 cells at 160 ASF are 0.893 and 0.446 lb-mole/hr, respectively. Other selected design values for the test facility are summarized in Table 6.1. Design point material balances for the 16 "A" cells and 16 "B" cells are given in Figures 6.2 and 6.3, respectively. The change in cell voltage with current density, consistent with Contract performance objectives, is given in Figure 6.4.

To conserve chemicals, the caustic and acid products from the cells were recombined on a continuous basis to form new sodium sulfate feed for the cells.

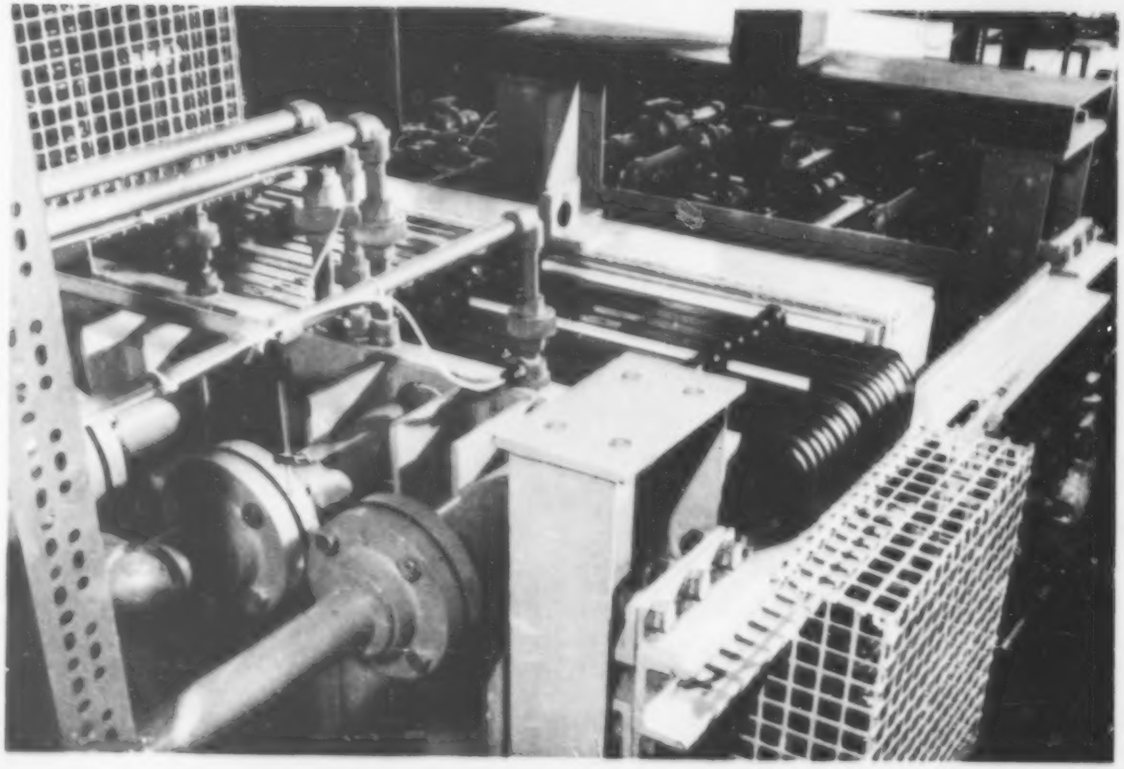


FIGURE 6.1 ASSEMBLED PROTOTYPE CELL STACK

TABLE 6.1

SELECTED DESIGN VALUES OF PROTOTYPE CELL TEST FACILITY

Cell Type	A	or	B
Active Area per Cell, sq ft	5		5
No. of Stacks	1		1
No. of Cells per Stack	16		16
Total Active Cells	16		16
Cells per Electric Module	8		8
Cells per Hydraulic Module	16		16
Design Current Density, ASF	160		160
Stack Current, amps	6400		6400
Maximum Cell Voltage, (a,b) volts	6.9		7.5
Maximum stack voltage, volts	13.8		15.0
Maximum total power, kw d-c	88.3		96.0
Maximum Design d-c Energy per lb NaOH (a,b), kwh/lb NaOH	2.47		2.68
Total Production, lb-mole/hr			
NaOH in mixed caustic	0.893		0.893
Low Sodium H_2SO_4	0		0.210
H_2SO_4 in mixed acid	0.446		0.236
Total Makeup Water (c)			
lb-mole/hr	0.689		12.52
GPM	0.025		0.451
Cooling Requirements (d)			
Anolyte, BTU/hr	109,000		117,000
Catholyte, BTU/hr	72,600		78,000
Cooling water (e) GPM	12.1		13.0

(a) Basis: 3N Na_2SO_4 feed solution, 85 percent NaOH C.E., 40 percent H_2SO_4 C.E., 140 F (60 C)

(b) Minimum Contract performance objective.

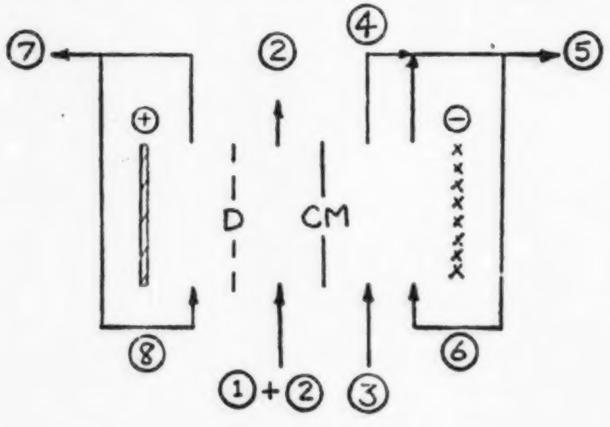
(c) Makeup water consists of water vaporized (140 F basis), electrolyzed, and, in the case of "B" cells, fed to the anolyte.

(d) Based on cell voltages (above) less 2 volt reversible voltage.
Sodium sulfate solution assumed fed at 120 F and makeup water account but heat losses to the environment neglected. Total cooling split 60-40, anolyte-catholyte.

(e) Based on 30 F temperature rise of cooling water.

Figure 6.2 Design Point Material Balance for 16 Prototype "A" Cells

	1		2		3		4		5		6		7		8		9		10	
	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
NaOH									35.7	.893	394	9.86								
Na_2SO_4	291	2.05	9.12	.0642	117.3	.826	9.12	.0642	117.3	.826	1294	9.12	228	1.603	3820	26.9				
H_2SO_4													43.6	.446	732	7.47				
H_2O Liquid	963	53.5	30.1	1.674	387	21.5	30.1	1.574	446	24.8	4932	274	875	48.6	14670	815				
H_2O Vapor									1.949	.1083			.976	.0542						
H_2									1.052	.526										
O_2													8.42	.263						
Totals	1254		39.2		504		39.2		602		6621		1156		19222					
GPM	2.04		.064		.822		.064		.89 (liq)		9.87		1.785(liq)		29.9					
Sp. Gr.	1.227		1.227		1.227		1.227		1.342(")		1.342		1.285(")		1.285					
Temp, °F	100		100-140		100		140		140		-140		140		-140					
Press, psia	—		—		—		—		17.0		—		17.0		—					
CFM, OPT	—		—		—		—		4.0(gas)		—		2.0(gas)		—					

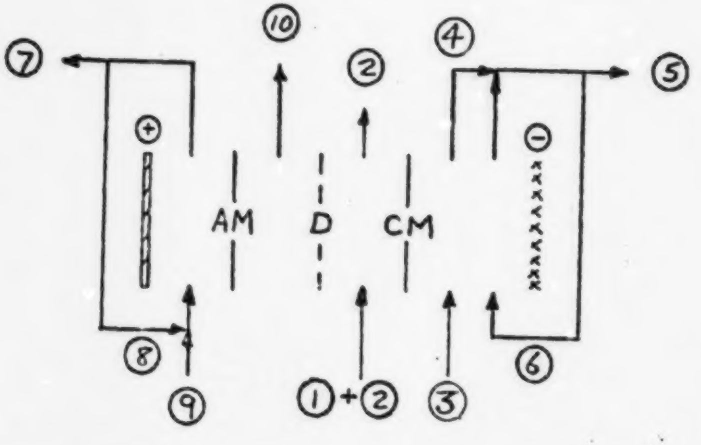


Basis:

16"A" Cells, 5.0 sq. ft. ea., 80 sq. ft.
Feed Normality = 4 N Na_2SO_4
Current Density = 160 ASF
NaOH Current Efficiency = 85 %
Purged H_2SO_4 Current Efficiency = N/A %
Operating Temperature = 40 °F
Catholyte Caustic Normality = 2 N
Anolyte Acid Normality = 1 N
Mid-Anolyte Acid Normality = N/A N

Figure 6.3 Design Point Material Balance for 16 Prototype "B" Cells

	1		2		3		4		5		6		7		8		9		10	
	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR	LB/HR	MOL/HR
NaOH									35.7	.893	394	9.86								
Na_2SO_4	291	2.05	9.12	.0642	117.3	.826	9.12	.0642	117.3	.826	1295	9.12							228	1.603
H_2SO_4													20.6	.210	1464	14.94			23.1	.236
H_2O Liquid	963	53.5	30.1	1.674	387	21.5	30.1	1.674	446	24.8	4932	274	202	11.25	14400	800	213	11.83	886	49.2
H_2O Vapor									1.949	.1083			.976	.0542						
H_2									1.052	.526										
O_2													8.42	.263						
Totals	1254		39.2		504		39.2		602		6621		232		15864		213		1137	
GPM	2.04		.064		.822		.064		.89 (liq)		9.87		.42 (liq)		29.9		.426		1.791	
Sp. Gr.	1.227		1.227		1.227		1.227		1.342 (")		1.342		1.061 (")		1.061		1.00		1.270	
Temp, ^{o}F	100		100-140		100		140		140		-140		140		-140		80		140	
Press, psia	–		–		–		–		17.0		–		17.0		–		–		–	
CFM, OPT	–		–		–		–		4.0 (gas)		–		2.0 (gas)		–		–		–	



Basis:

16 "B" Cells, 5.0 sq. ft. ea., 80 sq. ft.

Feed Normality = 4 N Na_2SO_4
Current Density = 160 ASF
NaOH Current Efficiency = 85 %
Purged H_2SO_4 Current Efficiency = 40 %
Operating Temperature = 140 ^{o}F
Catholyte Caustic Normality = 2 N
Anolyte Acid Normality = 2 N
Mid-Anolyte Acid Normality = 0.53 N

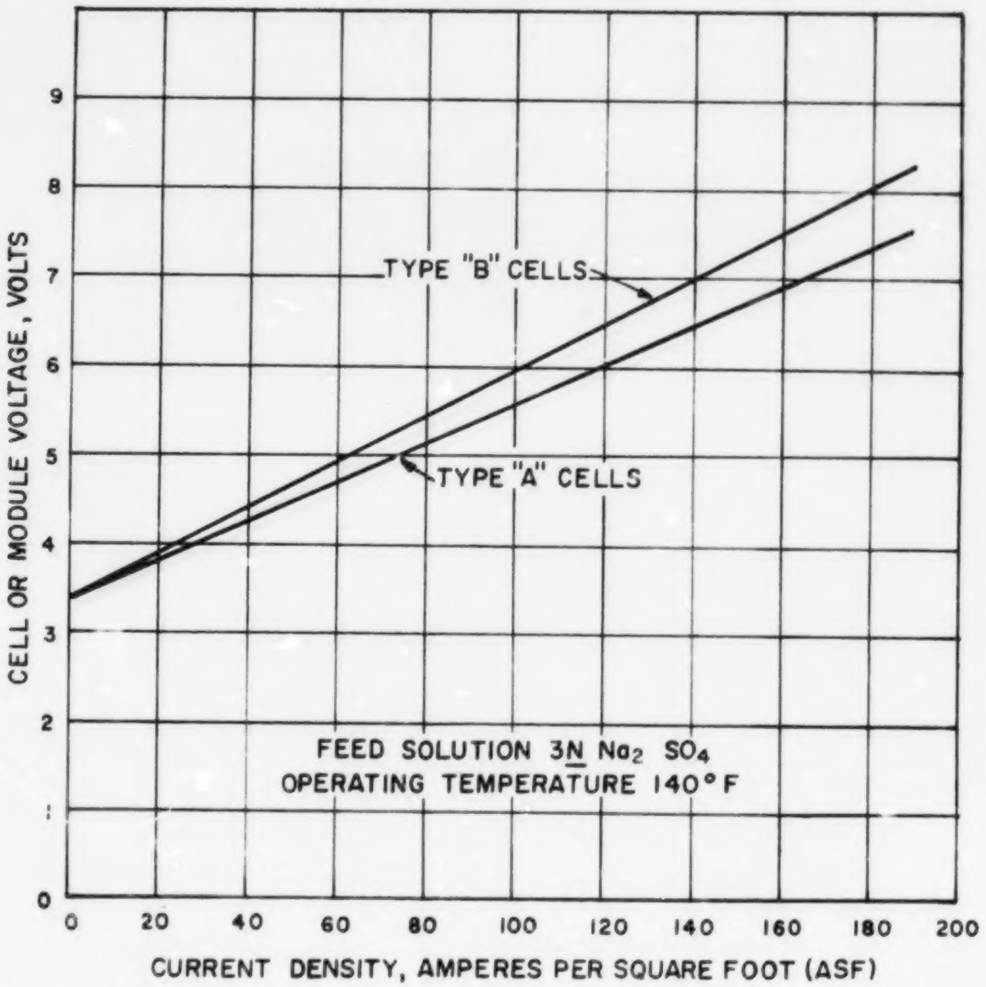


FIGURE 6.4 DESIGN CELL VOLTAGE-CURRENT DENSITY RELATIONSHIPS FOR TYPES "A" AND "B" SULFOMAT™ CELLS

VII

PROTOTYPE CELL PERFORMANCE

The performance of the prototype cells was measured in the test facility described in Sec. 3.0. Sixteen "A" cells were tested first, then sixteen "B" cells.

7.1 "A" CELL PERFORMANCE

7.1.1 Current Efficiency

Current efficiency measurements compare the actual amount of NaOH and H_2SO_4 produced by the cells to the theoretical amount that could be produced according to Faraday's law for the actual current applied to the cells. The current efficiency results for the sixteen prototype "A" cells in the test facility are summarized in Table 7.1. The table shows that the average current efficiencies for the catholyte and anolyte were 84 percent and 83 percent, respectively.* Furthermore, the current efficiencies at a current density of 160 ASF (C.E. Nos.13-16) averaged essentially the same as those at 120 ASF. Also, the current efficiencies at a sodium sulfate feed concentration of 3N were the same, as expected, as those at 2N.

7.1.2 Energy Consumption

The total d-c energy applied to the bus bars of the test facility divided by the production rate of caustic by the sixteen prototype "A" cells gives the overall specific energy consumption for caustic production, kwh/lb NaOH. Specific energy consumption results are included in Table 7.1 and are arranged according to Na_2SO_4 feed concentration and current density in Table 7.2.

The "Performance Objective" values in Tables 7.1 and 7.2 for the "NaOH DC Energy Factors" are based on the Phase I Performance Objectives (3N Na_2SO_4 Feed Solution, 140 F operating temperature, 85 percent NaOH current efficiency) but adjusted downward to reflect the actual current densities. The adjustment was made in accordance with the cell voltage—current density relationship given in Figure 6.4.

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*NOTE: The independently measured catholyte and anolyte current efficiencies must be equal for a given cell provided there are no undesirable side reactions at the electrodes and no external leakage of either product. Our prior experience with these cells indicates that the catholyte current efficiency may run slightly higher than the anolyte current efficiency due to anode side reactions.

Table 7.1

SUMMARY OF PERFORMANCE TESTS OF PROTOTYPE "A" CELLS

C.E. No.	Na_2SO_4 Feed Conc. N	Catholyte		Anolyte		Consistency Ratio(a) ($NaOH:H_2SO_4$)	Av. Op. Temp °F	Current		Bus Voltage volts	Cell Voltage		NaOH DC Energy Factors KWH/lb NaOH	
		NaOH Conc. N	C.E.	H_2SO_4 Conc. N	C.E.			Busbar amps	C.D. ASF		Actual[b] volts	Target[c] volts	Measured[d]	Performance Objective[e]
4	2.2	1.62	83%	1.04	79%	1.05	135	4770	119.3	10.4	5.2	6.01	1.92	2.15
5	2.2	1.62	91%	0.89	88%	1.03	136	4770	119.3	10.3	5.2	6.01	1.73	2.15
6	2.0	1.82	76%	0.95	78%	0.98	134	4770	119.3	10.6	5.3	6.01	2.12	2.15
7	2.0	1.86	76%	0.96	84%	0.90	134	4800	120.0	11.0	5.5	6.02	2.22	2.16
8	1.8	2.02	87%	1.09	77%	1.13	135	4800	120.0	11.0	5.5	6.02	1.91	2.16
9	1.9	1.85	94%	0.98	90%	1.04	135	4770	119.3	12.0	6.0	6.01	1.95	2.15
10	1.9	1.86	76%	0.99	82%	0.92	137	4875	121.9	12.6	6.3	6.07	2.51	2.17
11	2.0	1.89	89%	0.98	92%	0.98	135	4800	120.0	10.8	5.4	6.02	1.84	2.16
12	2.0	1.87	66%	0.98	81%	1.06	136	4800	120.0	11.2	5.6	6.02	1.97	2.16
13	1.9	1.92	85%	0.96	79%	1.08	137	6390	159.8	13.4	6.7	6.89	2.39	2.47
14	2.0	1.97	89%	1.02	83%	1.07	137	6390	159.8	13.0	6.5	6.89	2.23	2.47
15	3.0	2.40	81%	1.33	79%	1.03	140	6375	159.4	11.6	5.8	6.89	2.18	2.46
16	2.8	2.37	86%	1.29	76%	1.05	140	6405	160.1	11.3	5.6	6.90	2.14	2.47
17	2.9	2.27	84%	0.89	86%	0.97	137	4785	119.6	10.0	5.0	6.02	1.81	2.15
18	3.0	2.22	85%	0.96	87%	0.98	135	4800	120.0	10.2	5.1	6.02	1.82	2.16
		Av.	84%	Av.	83%									

---

a. Ratio of total equivalents of NaOH and H_2SO_4 involved in the C.E. Measurement.

b. Average cell voltage, i.e. bus voltage ÷ 2.

c. Calculated from $V_{a,target} = 5.469 \times 10^{-4} I_{a,bus} + 3.4$ which is plotted in Fig. 3.

d. Calculated from measured caustic production rate, DC busbar current and bus voltage

e. Phase I Performance Objective (3N Na_2SO_4 feed solution, 140° F operating temperature, 85% NaOH current efficiency) but adjusted downward in accordance with the cell voltage-current density relationship given in Fig. 3 to account for the above actual current densities.

TABLE 7.2

SUMMARY TO PROTOTYPE "A" CELL ENERGY CONSUMPTION DATA

Na_2SO_4 Feed Conc.	Current Density ASF	C.E. No.	NaOH DC Energy Factor	
			Measured	Performance Objective*
1.8 - 2.2N	120	4	1.92	2.15
		5	1.73	2.15
		6	2.12	2.15
		7	2.22	2.16
		8	1.91	2.16
		9	1.95	2.15
		10	2.51	2.17
		11	1.84	2.16
		12	1.97	2.16
		Av.	2.02	2.16
	160	13	2.39	2.47
		14	2.23	2.47
		Av.	2.31	2.47
2.8 - 3.0	120	17	1.81	2.15
		18	1.82	2.16
		Av.	1.82	2.16
	160	15	2.18	2.46
		16	2.14	2.47
		Av.	2.16	2.47

---

*Phase I Performance Objectives (3N Na_2SO_4 feed solution, 140 F operating temperature, 85 percent NaOH current efficiency) but adjusted downward in accordance with the cell voltage - current density relationship given in Figure 6.4 to account for the actual current densities.

Table 7.2 shows that, at both Na2SO4 feed concentrations and both current densities, the measured NaOH energy factors were within the performance objectives. At 2N Na2SO4 feed concentration, the measured energy factors were better than the performance objectives by 6.5 percent at both current densities. At 2.9N Na2SO4 feed concentration, the measured energy factors were better than the performance objectives by 12 percent and 16 percent at current densities of 160 ASF and 120 ASF, respectively.

7.1.3 Cell Voltage

Cell voltage as a function of current density was determined for the sixteen prototype "A" cells in the test facility with a Na2SO4 feed concentration of 2.9N and an operating temperature of 135–140 F. The results are plotted in Figure 7.1 together with the Contract performance objective curve for "A" cells, taken from Figure 6.4. The plotted cell voltage is the average voltage of the two electric modules into which the sixteen cells are divided in the test facility.

Figure 7.1 shows that the measured "A" cell voltages are significantly lower than the target performance objective voltages at all current densities covered by the measurements. Also, the figure shows that the voltage–current density curve is essentially linear in the current density range of practical interest (80 to 160 ASF) with a zero–current intercept of 3.4 volts.

7.2 "B" CELL PERFORMANCE

7.2.1 Cell Voltage

Cell voltage as a function of current density was determined for the sixteen prototype "B" cells in the test facility with a Na2SO4 feed concentration of 2N, and an operating temperature of 135–140 F. The results are plotted in Figure 7.2 together with the Contract performance objective curve for "B" cells, taken from Figure 6.4. The plotted cell voltage is the average voltage of the two electric modules into which the sixteen cells are divided in the test facility.

Figure 7.2 shows that the measured "B" cell voltages are significantly lower than the target performance objective voltages at all current densities covered by the measurements. Also, the Figure shows that the voltage–current density curve is essentially linear in the current density range of practical interest, i.e., above 80 ASF.

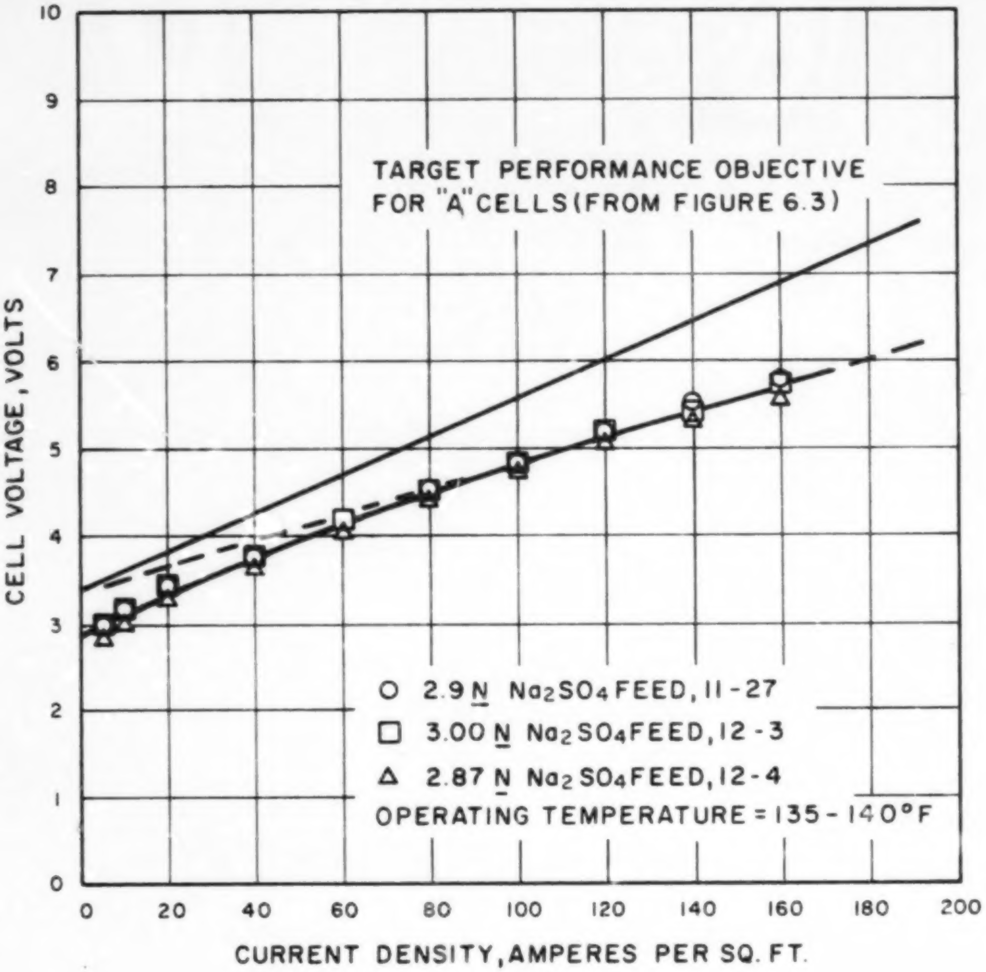

FIGURE 7.1 CURRENT - VOLTAGE CURVE FOR PROTOTYPE "A" CELLS

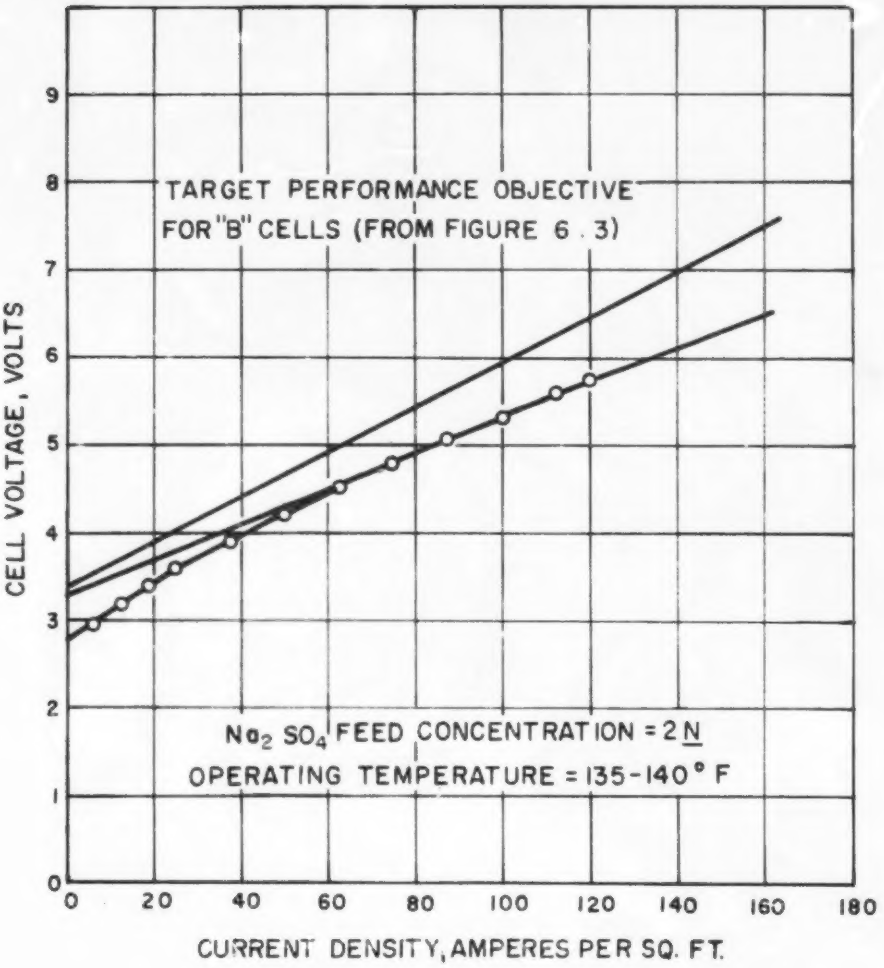

FIGURE 7.2 CURRENT-VOLTAGE CURVE FOR PROTOTYPE "B" CELLS

7.2.2 Current Efficiency and Energy Consumption

As originally assembled, the current efficiencies of the prototype "B" cells were relatively low due to the presence of crossleaks.

Corrective measures were taken by hand revising some components of two cells. Tests with the revised cells showed improved performance as shown in Table 7.3.

The table shows that the measured NaOH energy factors were within the performance objectives. At current densities of 90 and 125 ASF, the measured energy factors were better than the performance objectives by 1 and 2 percent, respectively. At 150 ASF, the measured energy factors were better than the performance objectives by an average of 10 percent.

In addition, the "B" anolyte current efficiencies of Table 7.3 averaged 42 percent. This also met the performance objective for the current efficiency of purge sulfuric acid.

Table 7.3

SUMMARY OF PERFORMANCE TESTS OF PROTOTYPE "B" CELLS

C.E. No.	Na_2SO_4 Feed Conc. N	Catholyte		Mid-Anolyte		Anolyte		Total Acid C.E.	Consistency Ratio[a/] ($NaOH:H_2SO_4$)	Av. Op. Temp °F	Current Density ASF	Cell Voltage volts	NaOH DC Energy Factors	
		NaOH Conc. N	C.E.	H_2SO_4 Conc. N	C.E.	H_2SO_4 Conc.	C.E.						Measured[b/]	Performance Objective[c/]
													KWH/lb NaOH	
B1	3.1	2.17	84%	0.51	36%	2.19	45%	81%	1.04	128	150.0	6.3	2.33	2.59
B2	3.3	2.49	80%	0.83	37%	2.34	41%	79%	1.02	134	151.0	6.2	2.44	2.60
B3	3.6	2.52	79%	0.60	36%	2.21	42%	77%	1.03	118	125.3	5.9	2.32	2.37
B4	3.2	2.45	75%	0.77	40%	2.07	38%	76%	0.96	100	90.2	5.1	2.02	2.04
B5	3.5	2.12	80%	0.73	39%	2.13	42%	82%	0.98	123	149.7	6.0	2.19	2.59
B6	3.5	2.55	80%	0.74	36%	2.26	43%	79%	1.01	124	150.0	6.1	2.38	2.59

a/ Ratio of total equivalents of NaOH and H_2SO_4 involved in the C.E. Measurement.

b/ Calculated from measured caustic production rate, DC busbar current and bus voltage.

c/ Phase I Performance Objective (3N Na_2SO_4 feed solution, 140° F operating temperature, 85% NaOH current efficiency) but adjusted downward in accordance with the cell voltage-current density relationship for "B" cells given in Figure 3 to account for the above actual current densities.

PHASE IC
PROTOTYPE PLANT COST ESTIMATE, PROJECTED OPERATING COSTS, AND DESIGN AND CONSTRUCTION SCHEDULE FOR PROTOTYPE PLANT

I

GENERAL DESCRIPTION OF PROCESS WORK

The SWEC/Ionics SO2 Removal Unit is designed to continuously desulfurize boiler stack gas from WEPCO Valley Plant boilers 3 or 4. The process for removal of SO2 from stack gases is a closed system using electrolytic regeneration of basic process liquids, caustic soda and sulfuric acid. Absorption of flue gas SO2 is accomplished in a process tower using recycle caustic soda as the absorption medium and forming sodium compounds. Tower bottoms consisting of these sodium compounds are reacted with dilute recycle sulfuric acid which releases SO2 and forms sodium sulfate. SO2 is then stripped from the sodium sulfate in a stripper tower and the sodium sulfate processed in an electrolytic cell to produce caustic soda and sulfuric acid. These basic process liquids are recycled to the process streams.

The SWEC/Ionics process unit for SO2 removal therefore consists of an absorption/stripping section and an electrolytic cell section plus necessary ancillary process equipments as shown in the Figure I in the Executive Summary.

Design of a SO2 Prototype Removal Unit was based on the results of the SO2 Removal Pilot Plant.

II

COST ESTIMATE FOR SWEC/IONICS SO2 REMOVAL UNIT FOR WEPCO 75 MW POWER PLANT

Development of the cost estimate for the SWEC/Ionics SO2 Removal Unit for WEPCO's 75 MW Valley Power Plant given in the Cost Summary Sheets is summarized as follows:

2.1 Design Basis Cost Summary Sheet Dated 8/22/74

This cost represents an optimized chemical process with modification to front-end process equipments for lowered costs. The cost estimate, excluding escalation, contingency and fee is $14,475,000. This cost provides for an SO2 Removal Unit for a 75 MW Plant which includes:

A. A 4250 lb/hr SO2 removal capacity from boiler stack gas

B. A two-story cell system building

C. Automated cell room system with automatic control valves

D. SO2 drying and storage system

2.2 Design Basis 3100 lb/Hr SO2 Removal Unit Cost Summary Sheet Dated 11/18/74 – Alternate to 8/22/74 Summary

This cost is for a 3100 lb/hr SO2 Removal Unit alternate SO2 Removal Unit with reduced size equipment. The cost estimate, excluding escalation, contingency and fee is $12,229,563. This cost provides an alternate, smaller SO2 Removal Unit. The cost reflects a tightened design basis for the SO2 Removal Unit with cell room design of:

A. 3100 lb/hr SO2 regeneration capacity

B. Reduction of capacity of equipment items for 3100 lb/hr design basis

C. Subsitution of semiautomatic system in cell room requiring greater operator attention during start-up and shutdown

It should be noted that the cost of the 4250 lb/hr Unit and the 3100 lb/hr Unit include the costs of:

A. The Q-213 Dilute Acid Storage Tank ($261,720) (WEPCO holding tank for accumulation for shipping, or for WEPCO dilute acid use) and

B. The SO2 drying and storage system ($1,127,000).

Table 2.1

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PROCESS PLANT COST SUMMARY
A8180 16 (FRONT)

J.O. W.O.	12302.03
CLIENT	WISCONSIN ELECTRIC VALLEY PLANT, MILW., WISCONSIN
DATE	REV 8-22-74
PROJECT	SO_2 REMOVAL PLANT: SUMMARY SHEET 4250 #/hr Removal
BY	R.H.B.
CHKD	

ACCT	DESCRIPTION	NO PCS	FACTORS DM*	FACTORS IM	MATERIAL	LABOR	TOTAL	MAN-HOURS
	PROCESS EQUIPMENT							
A	TOWERS				544,250	3,100	547,350	365
B	BOILERS & HEATERS							
F	PROCESS FURNACES							
G	GENERAL EQUIPMENT				358,300	52,000	410,300	5,775
L	REACTORS				2,100,000	172,400	2,272,400	19,155
M	DRUMS				138,400	4,800	143,200	550
Q	STORAGE TANKS				251,650	4,000	255,650	470
P	PUMPS (INCLUDING DRIVES)				127,600	17,000	144,600	2,000
R	COMPRESSORS (INCLUDING DRIVES)				160,000	20,400	180,400	2,350
S	STACKS							
T	HEAT EXCHANGERS				218,700	2,900	221,600	320
	TOTAL PROCESS EQUIPMENT				3,898,900	276,600	4,175,500	30,985
	PROCESS MATERIALS							
C	PIPING				830,000	850,000	1,680,000	93,407
D	STRUCTURES				160,000	50,000	210,000	5,495
E	ELECTRICAL			S/C	1,080,000	1,070,000	2,150,000	54,844
H	BUILDINGS				858,000	420,000	1,278,000	7,195
J	CIVIL				130,000	98,000	228,000	12,744
K	INSTRUMENTS				375,000	150,000	525,000	16,251
W	INSULATION			S/C	334,000	-	[illegible]	
N	PAINTING			S/C	100,000	-	[illegible]	
					50,000	-	50,000	-
	TOTAL PROCESS MATERIALS				3,917,000	2,638,000	6,555,000	229,936
	TOTAL DIRECT COST (DM* + DL)				7,815,900	2,914,600	10,730,500	260,921
	DISTRIBUTABLE ACCOUNTS							
V1	INSURANCE (EXCLUDING ALL RISK)					65,000	65,000	
V2	FEDERAL AND STATE TAXES					186,000	186,000	
X	TEMPORARY CONSTRUCTION FACILITIES				90,300	21,400	111,700	2,685
Y	FIELD OFFICE (INCLUDING INSURANCE AND TAXES)				14,900	361,200	376,100	
Z	CONSTRUCTION TOOLS AND EQUIPMENT				421,200	94,700	515,900	11,850
O	OTHER DISTRIBUTABLE ITEMS				6,500	551,100	557,600	15,000
	TOTAL DISTRIBUTABLE				532,900	1,279,400	1,812,300	29,535
	SUBTOTAL - COST OF WORK				8,348,800	4,194,000	12,542,800	290,456
U	INDIRECT ACCOUNTS							
	ENGINEERING				109,700	419,700	529,400	36,300
	DESIGN					470,600	470,600	50,620
	OTHER HEADQUARTERS OFFICE				84,400	94,000	178,400	10,045
	TAXES - HEADQUARTERS PAYROLL					64,700	64,700	
	OVERHEAD ALLOWANCE				689,100		689,100	
	TOTAL INDIRECT (HEADQUARTERS OFFICE)				883,200	1,049,000	1,932,200	96,965
	TOTAL PRESENT DAY PRICES				9,232,000	5,243,000	14,475,000	
	ESCALATION							
	EXTENDED WORK WEEK							
	TOTAL COST EXCLUDING FEE AND CONTINGENCY							
	ESTIMATE OF SUBCONTRACT COSTS INCLUDING ABOVE							

FOR ITEMS INCLUDED OR EXCLUDED FROM THE ESTIMATE SEE OTHER SIDE

Table 2.2

PROCESS PLANT COST SUMMARY
[illegible] (FRONT)

CLIENT WISCONSIN ELECTRIC POWER COMPANY, MILWAUKEE, WISCONSIN	J.O. 12302.03 W.O. F.-
PROJECT INTEGRATED SO_2 REMOVAL PLANT: SUMMARY SHEET 3100 ¢/hr Removal	DATE NOV 18, 1974
	BY R. BAUER CHKD

SECT.	DESCRIPTION	NO. PCS	FACTORS %DM	FACTORS L'M	MATERIAL	LABOR	TOTAL	MAN-HOURS
	PROCESS EQUIPMENT							
A	TOWERS							
B	BOILERS & HEATERS				544,250	3,100	547,350	365
F	PROCESS FURNACES				-	-	-	-
G	GENERAL EQUIPMENT				-	-	-	-
L	REACTORS				162,800	38,400	201,200	4,263
N	DRUMS				-	-	-	-
Q	STORAGE TANKS				96,700	3,400	100,100	394
P	PUMPS (INCLUDING DRIVES)				105,550	2,000	107,550	230
R	COMPRESSORS (INCLUDING DRIVES)				81,000	10,500	91,500	1,232
S	STACKS				142,800	18,200	161,000	2,092
T	HEAT EXCHANGERS				-	-	-	-
	IONICS CELL INSTALLATION		S/C		182,500	2,000	186,500	224
	TOTAL PROCESS EQUIPMENT				3,402,063	-	3,402,063	-
	PROCESS MATERIALS				4,717,663	77,600	4,795,263	8,800
C	PIPING							
D	STRUCTURES				445,000	523,000	968,000	57,470
E	ELECTRICAL				146,800	46,500	193,300	5,105
H	BUILDINGS		S/C		1,457,700	-	1,457,700	-
J	CIVIL				532,200	240,300	772,500	27,200
K	INSTRUMENTS				129,500	96,900	226,400	12,601
N	INSULATION				241,800	53,100	294,900	5,751
[illegible]	[illegible]		S/C		304,700	-	304,700	-
	[illegible]		S/C		[illegible]		[illegible]	-
			[illegible]		[illegible]		[illegible]	-
	TOTAL PROCESS MATERIALS				3,392,700	959,800	4,352,500	108,127
	TOTAL DIRECT COST (DM* + DL)				8,110,363	1,037,400	9,147,763	116,927
	DISTRIBUTABLE ACCOUNTS							
VI	INSURANCE (EXCLUDING ALL RISK)				-	37,100	37,100	
VS	FEDERAL AND STATE TAXES				-	106,200	106,200	-
X	TEMPORARY CONSTRUCTION FACILITIES				77,200	18,200	95,400	-
Y	FIELD OFFICE (INCLUDING INSURANCE AND TAXES)				14,900	334,200	349,100	2,285
Z	CONSTRUCTION TOOLS AND EQUIPMENT				244,900	61,600	306,500	-
O	OTHER DISTRIBUTABLE ITEMS				6,300	368,700	375,000	7,700
								16,370
	TOTAL DISTRIBUTABLE				343,300	926,000	1,269,300	26,355
	SUBTOTAL—COST OF WORK				8,453,663	1,963,400	10,417,063	143,282
U	INDIRECT ACCOUNTS							
	ENGINEERING				109,700	398,820	508,520	34,500
	DESIGN				w/Engr.	424,050	424,050	45,600
	OTHER HEADQUARTERS OFFICE				84,400	94,000	178,400	10,045
	TAXES - HEADQUARTERS PAYROLL				-	59,600	59,600	-
	OVERHEAD ALLOWANCE				641,900	-	641,900	-
	TOTAL INDIRECT (HEADQUARTERS OFFICE)				836,000	976,500	1,812,500	90,145
	TOTAL, PRESENT DAY PRICES				9,289,663	2,939,900	12,229,563	
	ESCALATION							
	EXTENDED WORK WEEK							
	TOTAL COST, EXCLUDING FEE AND CONTINGENCY							
	ESTIMATE OF SUBCONTRACT COSTS INCLUDING ABOVE							

FOR ITEMS INCLUDED OR EXCLUDED FROM THE ESTIMATE, SEE OTHER SIDE

III

PROJECTED MONTHLY OPERATING COSTS

A cost estimate was generated for monthly operating costs for the first year of Phase III operation of the 75 MW Demonstration (Prototype) Plant. Both SWEC and WEPCO labor will be used to conduct tests throughout the year. Graduate Engineers including a supervisor will constitute the SWEC labor requirement. Test equipment and material costs have been included in the estimate along with the utilities and needed chemicals.

The SWEC/Ionics process generates dilute sulfuric acid and hydrogen as well as the SO2 removed from the stack gasses. These streams, and return of condensate used in the stripper reboiler to the power plant, have been considered to have an economic value favorable to the SWEC/Ionics process. A credit for these streams has therefore been factored into the operating and maintenance cost estimate. The total monthly operating and maintenance costs for each month of the first year's operation is tabulated in Table 3.1 which shows that when the year test period is concluded and SWEC test/operating labor are no longer required, the SO2 Removal Unit can provide an income as a result of the SWEC/Ionics process.

TABLE 3.1

ESTIMATE OF OPERATING AND MAINTENANCE COSTS - 75 MW DEMONSTRATION PLANT FOR 3,100 LB/HR SO2 REMOVAL (NOTE 1)

PROTOTYPE PLANT OPERATION PHASE III

Months:	January	February	Typical for Each Month (Mar,Apr,May)	Typical for Each Month (June,July,Aug)	Typical for Each Month (Sept,Oct,Nov)	December
OPERATING LABOR						
Supervisory Personnel (S&W) (Note 2)	$ 53,375.00	$ 53,375.00	$ 53,375.00	$ 53,375.00	$ 53,375.00	$ 45,750.00
WEPCO Operators at $48,000/Yr, 3 Shifts (1 Man/Shift)	8,000.00	8,000.00	8,000.00	4,000.00	4,000.00	4,000.00
MAINTENANCE						
For S&W Section at 4% of Fixed Capital Investment (Note 3)	19,150.00	19,150.00	19,150.00	19,150.00	19,150.00	19,150.00
For Ionics Section (Note 4)	24,167.00	24,167.00	24,167.00	24,167.00	24,167.00	24,167.00
UTILITIES						
Water						
Cooling MM Gal at $0.116/1,000	6.8MM/ $789.00	10.2/ $1,183.00	14.9/ $1,728.00	20.1/ $2,332.00	14.9/ $1,728.00	13.6/ $1,578.00
Deionized MM Gal at $1.00/1,000	508.00	762.00	952.00	952.00	952.00	952.00
Steam Tons at $0.67/1,000 lb (Note 5)	1,640.00	2,460.00	3,279.00	3,279.00	3,279.00	3,279.00
Electricity						
Cells 4,500 Kw at $0.00781/Kwhr	10,250.00	15,354.00	20,501.00	20,501.00	20,501.00	20,501.00
Other Equipment 1,433 Kw at $0.00781/Kwhr	6,528.00	6,528.00	6,528.00	6,528.00	6,528.00	6,528.00
Tests and Inspection at $0.50/Ton SO2	225.00	337.00	450.00	450.00	450.00	450.00
PLANT ADMINISTRATION (Note 6)	20,000.00	20,000.00	20,000.00	20,000.00	20,000.00	20,000.00
CHEMICALS						
50% (wt) Caustic Soda at $85/Ton	11 Tons/ $935.00	7/$595.00	8/$680.00	8/$680.00	8/$680.00	8/$680.00
93% (wt) Sulfuric Acid at $33/Ton	7.2 Tons/ $238.00	4.2/$1[illegible].00	4.8/$158.00	4.8/$158.00	4.8/$158.00	4.8/$158.00
35 wt% Hydrogen Peroxide at $300/Ton (Note 7)	551.00	592.00	762.00	762.00	762.00	762.00
Filter Aid Material at $135/NT	123.00	132.00	170.00	170.00	170.00	170.00
ESTIMATED CREDITS						
Condensate from Stripper Reboiler (Note 8)	(140.00)	(200.00)	(280.00)	(280.00)	(280.00)	(280.00)
Dilute Sulfuric Acid (Note 9)	(3,625.00)	(5,438.00)	(7,250.00)	(7,250.00)	(7,250.00)	(7,250.00)
Hydrogen (Heating Value) (Note 10)	(990.00)	(1,485.00)	(1,979.00)	(1,979.00)	(1,979.00)	(1,979.00)
Sale of Liquid SO2 (Note 11)	(24,989.00)	(37,483.00)	(49,952.00)	(49,952.00)	(49,952.00)	(49,952.00)
	(29,774.00)	(44,606.00)	(59,461.00)	(59,461.00)	(59,461.00)	(59,461.00)
TOTAL MONTHLY OPERATING AND MAINTENANCE COSTS						
(Less Credits)	146,479.00	152,774.00	159,900.00	156,504.00	155,900.00	148,125.00
(With Credits)	116,735.00	108,168.00	100,439.00	97,043.00	96,439.00	88,664.00

TYPICAL NORMAL OPERATION O&M COST/MONTH
(With Credits and Less S&W Test Labor)
$97,043.00 - $53,375.00 = $43.668.00

See footnotes next page.

Notes to Table 3.1

1) Costs predicated on 3,100 lb/hr SO_2 removal on continuous basis. Capability for 4,250 lb/hr SO_2 removal peaking capacity for 33 hr is incorporated into plant design. Second quarter 1974 prices.

2) Costs include salary and per diem for a 30 and 1/2 day month, 7 day per week operation. One chief operator, four operating advisors (four men covering 24 hours), one chemist, and one process engineer. Two additional man-months should be included for report writing for months 13 and 14.

3) Costs predicated on basis of 3,100 lb/hr SO_2 removal capital costs estimate and excludes escalation, contingency, and fee.

4) Monthly costs based on cell maintenance materials yearly cost of $210,000 plus cell system maintenance of $80,000 per year.

5) Cost is for steam rate of 8,370 lb/hr for an average 583 hr month (2,447 tons per month), except for start-up in months 1 and 2.

6) Plant taxes and plant insurance are not included due to diversity in plant locations and accounting methods.

7) Based on yearly cost of $9,150 for 30 and 1/2 tons at $300/ton.

8) Credit based on return of condensate to power plant at rate of approximately 8 gpm and cost of $1.00 per 1,000 gal. (Total $3,320/year)

9) Credit for use of dilute H_2SO_4 by power plant for treating demineralizers on 100% basis. Rate of 0.356 tons/hr (100% basis) at $35/ton. (Total $87,220/year).

10. Credit for use of H_2 as fuel (heating value). 3.9 MM Btu/hr, $0.87/MM Btu (LHV) (Total $24,000/year)

11. Credit for the sale of SO_2. Credit based on 2,635 lb/hr x 7,000 = 9,223 tons/year. Current market price for SO_2 is $110/ton. Arbitrary conservative price of $65/ton used for this estimate.

IV

DESIGN, ENGINEERING, AND CONSTRUCTION SCHEDULE FOR WEPCO 75 MW UNIT

The proposed schedule for installing the 75 MW demonstration at the WEPCO Valley Station site appears as Figure 4.1. The schedule extends over the estimated 28 months required to reach mechanical completion from the date of Contract Award. Upon reaching mechanical completion, the Operating and Test Program described under Phase ID would begin.

Figure 4.1

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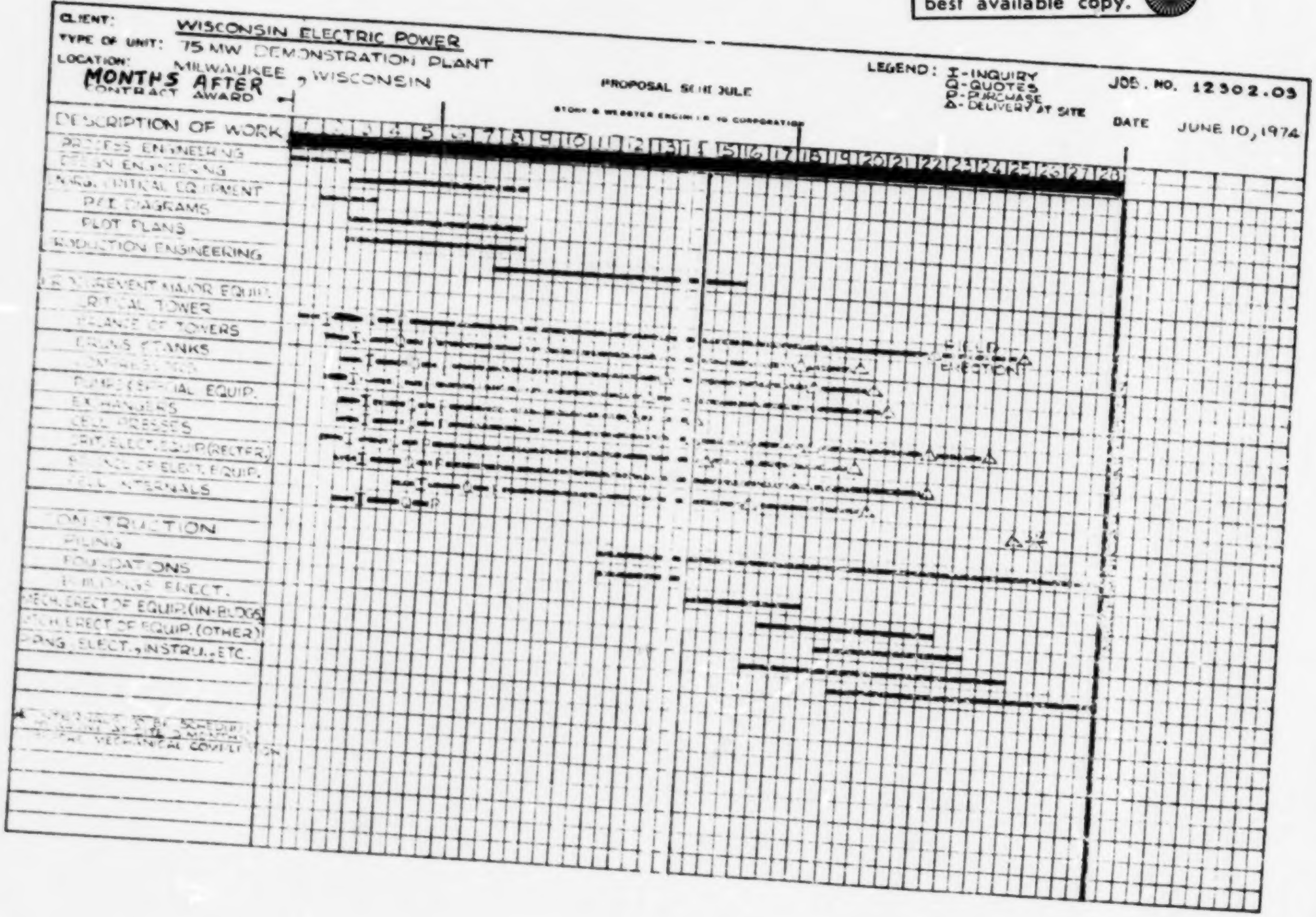

PHASE ID

TEST PROGRAM AND OPERATING SCHEDULE FOR 75 MW PROTOTYPE PLANT

I

INTRODUCTION

This test program and operating schedule is intended as a supplement to the Test Program and Operating Schedule Manual prepared for the Pilot Plant Test Program under EPA contract No. 68-02-0297. This schedule specifies the differences between the 75 Mw Demonstration Test Program and the Pilot Plant Test Program.

During the Pilot Plant Program, it was possible to vary some operating conditions in the absorption section. In the demonstration plant, it will not be possible to vary absorption conditions in a predetermined manner. The demonstration plant operating conditions will largely be determined by the prevailing operation of WEPCO No. 4 boiler.

The Test Program for the demonstration plant will necessarily be limited in scope. The Test Program is primarily directed toward the evaluation of process technical performance on a larger scale, determination of process economics, process availability, and maintainability.

II

TEST PROGRAM OBJECTIVES

A summary of the major test program objectives, excluding the Electrolytic Section, is presented in Table 2.1. The test program for the Electrolytic Section will be similar to the program as detailed in the Pilot Plant Test Program and Operating Schedule Manual.

2.1 PROCESS PERFORMANCE

It will be important to establish the process material balance at an early date. This will help to identify and quantify system chemical losses.

This time will also allow for:

1. Checking accuracy of instrumentation
2. Familiarization with analytical procedures
3. Technical personnel training period

2.2 ABSORPTION SECTION

Pilot plant operation indicated a problem with closure of the system water balance. One explanation for the lack of closure may have been that the inlet flue gas was not completely saturated in the quench section. Should a similar condition occur in the demonstration plant, it is planned to take humidity measurements of the gas before and after the quench section.

Entrainment, if any, of process liquor in the absorber overhead will be more closely followed. It is planned to follow the same measurement technique as used by EPA in the pilot plant determination.

Oxidation of SO_2 in the absorber was found to be relatively insensitive to those variables studied in the pilot plant, except for stage recirculation rates. The demonstration plant will have less holdup than the pilot plant; i.e., the packing volume per cubic foot of gas will be 50 percent of that used in the pilot plant.

In the demonstration plant, it is proposed to explore more closely:

1. The effect of NOx on oxidation
2. The effect of heavy metal cations on oxidation
3. The amount of SO_3 contained in the gas that contributes to the overall oxidation
4. The effect of flue gas O_2 concentration
5. The NOx removal capabilities of the system

TABLE 2.1

TEST PROGRAM OBJECTIVES

TASK	DATA REQUIRED
I. Establish process material balance and identify process chemical losses	1. Flue gas flow 2. SO2 concentration to and from absorber 3. Recycle acid-caustic flows and compositions 4. Process liquor losses and concentrations 5. Quantity and composition of recovered SO2 6. Tank inventories 7. Amount of oxidation 8. Weak acid production rate and concentration
II. Absorption Section	
1. Establish water balance on scrubber	1. Gas moisture content before and after quench section, gas temperatures
2. Measure entrainment from scrubber 3. Measure SO2 removal efficiences 4. Measure flue gas system pressure drops 5. Demonstrate feed-forward control system on caustic flow for maintaining desired SO2 exit concentration.	2. As defined by EPA procedure
6. Oxidation	6.
a. Determine amount of SO2 removal and oxidation in each packing stage	a. SO2 concentrations in gas phase to and from each stage Liquor analyses to and from each stage
b. Monitor concentration of trace heavy metals in feed/effluent of absorber	b. Appropriate liquor samples for Cu+2, Fe+2, Al+3
c. Monitor NOx to and from scrubber d. SO302 concentrations in feed gas	
7. Determine effectiveness of hydroclones for removing particulate matter from quench water	7. Solids concentration of inlet/outlet streams
III. Stripping-Recovery Sections	
1. Determine minimum stripping steam rate vs SO2 concentration and pH in bottoms	1. Steam, reflux and feed rates concentration of SO2 and H2SO4 feed liquor composition pH of bottoms stream temperatures
IV. Feed Liquor Treatment	
1. Establish optimum peroxide consumption	1. SO2 and Fe concentrations
2. Establish cycle time, pre-coat type and quantity, body aid feed quantity for removal of Fe/Al hydroxides.	
V. Process Characterization Factors	
1. Operator requirements and costs	
2. Maintenance requirements and costs	
3. Establish utilities and chemical make-up requirements.	

2.3 STRIPPING SECTION

The most important variable in this section is the minimum amount of steam necessary for a given concentration of SO2 in the stripped cell feed liquor.

As indicated during the pilot plant operation, the remaining SO2 in the stripped solution must be oxidized with hydrogen peroxide. If this is not done, divalent iron will not be oxidized to trivalent iron for subsequent removal as the hydrous oxide. Complete iron removal is necessary to maintain satisfactory cell operation.

Minimum steam consumption versus SO2 concentration in the cell feed liquor will be measured. The economic optimum SO2 concentration in the stripped solution will then be determined.

2.4 FEED LIQUOR TREATMENT

Iron and aluminum will be removed as the hydrous metal oxides on a pressure leaf, precoat type filter. Cycle times, solids loading, body and feed concentration, and the specific flow rate will be optimized based on the field operation.

Selection of the proper filter aid will be determined by field testing.

2.5 DATA COLLECTION AND EVALUATION

2.5.1 Technical Program

Data collection in the demonstration plant operation will be similar to the pilot plant operation.

Additional effort will be placed on obtaining more data in the following areas:

1. Sodium/sulfate ratios in absorber feed and draw liquors
2. SO2 gas phase inlet/outlet and interstage concentrations
3. SO3 concentration in flue gas
4. Absorber entrainment

Determination of the height of a transfer unit in the absorber bottom stage will be done by integrating the mass transfer equation. The equilibrium curve—operating lines are not straight over the concentration range in the bottom section. In the second stage, the mass transfer coefficient may be found more simply by assuming linear relations for the equilibrium-operating lines.

As was done in the evaluation of pilot plant data, we shall use the Stone & Webster Regression Analysis Program for data fitting. A multiple regression analysis routine is also available.

Normal data evaluation will specify a 95 percent confidence belt, unless it is decided to broaden or narrow the limits after analyzing the data.

2.5.2 Process Maintenance

The following information will be recorded in connection with maintenance requirements:

1. Number and types of WEPCO personnel
2. Subcontractor labor
3. Materials cost
4. Man-hours by craft category and supervisory requirement

2.5.3 Process Operating Costs

Detailed records shall be maintained to properly record all operating costs. Areas that are to be monitored are:

1. Raw materials - caustic soda, sulfuric acid, filter aid
2. Productive labor - operating personnel
3. Manufacturing expenses - water, steam, electricity
4. Other expenses - waste disposal, tests and inspections, plant transportation, and taxes